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ATTACHMENT B

A THEORETICAL EVALUATION OF THE EFFECTIVENESS OF CAPPING PCB CONTAMINATED NEW BEDFORD HARBOR BED SEDIMENT, DRAFT

(2397D)

SDMS DocID 62913

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A THEORETICAL EVALUATION OF THE EFFECTIVENESS OF CAPPING PCB CONTAMINATED NEW BEDFORD HARBOR BED SEDIMENT

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October 9, 1989
Balsam Project 6292.01

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PREFACE

This study was conducted as part of the Balsam Environmental Consultants, Inc. Project No. 6292.01 entitled: Proposed New Bedford Harbor Sediment Contaminant Containment Cap Evaluation. Project managers for Balsam were Weldon S. Bosworth and Leonard C. Sarapas, Salem, NH. The study was conducted during the period of August 1988 to October 1989 by Louis J. Thibodeaux, Baton Rouge, LA. with the assistance of Danny D. Reible also of Baton Rouge, LA. The word processor was Joyce Thibodeaux.

PART 1: INTRODUCTION

The existence of contaminated bed sediment in a natural aquatic system usually results in the overlying water column receiving some contamination from this source. Once in the water the volatiles easily enter the air. Therefore, a bed sediment source of contamination can lead to multimedia environmental exposure pathways.

Bed sediments have the ability to attract and hold considerable quantities of selected chemicals when being subjected to pollutant insults in the water column or when directly exposed. When the insults have ceased, the sediments then become a long term, low level source of chemical contamination to the water column. This is particularly true of those surface sediment layers nearest the water column. However, it is theoretically possible to employ the high adsorptive capabilities of the sediment coupled with low effective transport properties in an engineered and managed in-situ capping operation to effectively isolate the source of contamination from the biosphere.

This report provides the theoretical basis for the in-situ containment of the PCBs in the Upper Estuary of New Bedford Harbor by capping the contaminated sediment with much cleaner sediment. The effectiveness of a proposed capping scheme is evaluated. An engineering analysis is performed to assess the present release rate of PCBs. The analysis is then extended to consider the effectiveness of capping. Effectiveness is computed as the reduction in steady state chemical transport to the water column before and after capping.

PART II: TRANSPORT OF PCBS FROM BED SEDIMENT TO WATER COLUMN

This section of the report presents the methodologies used to calculate the current (i.e., 1985-86) rate at which Aroclors 1016/1242 and 1254 are being released from the bed sediment of the Upper Estuary of New Bedford Harbor into the overlying water. For simplicity Aroclors which are easily misidentified as Aroclor 1016 or 1242 because of similar composition and weathering will be referred to solely as A-1242 hereafter. Using field data along with physical, chemical and biological parameters mathematical models were developed to predict the

PCB flux rates. Model predictions were compared with field measurements reported by other investigators to arrive at estimated PCB flux rates.

TRANSPORT MECHANISMS IN BED SEDIMENT

There are numerous transport mechanisms within bed sediment that, if active, can be responsible for the movement of polychlorinated biphenyl molecules through the sediment water interface and into the water. Those mechanisms likely active in the New Bedford Harbor Upper Estuary were reviewed and evaluated. A total of ten processes/mechanisms were identified that could possible effect PCB fate in the sediment. Briefly these are:

a) absorption/desorption between solid and porewater (*),
b) molecular diffusion within porewater (*),
c) advective transport due to infiltration and recharge (XX),
d) sediment deposition/resuspension (*),
e) advective transport due to sand ripple/wave effect (XX),
f) bioturbation (*),
g) chemical reaction (XX),
h) biodegradation (X),
i) Brownian diffusion of colloidal particles (?) and
j) advection of colloidal particles (XX).

Order-of-magnitude numerical calculations were performed and the literature consulted in an effort to isolate the dominant processes/mechanisms. Those denoted by XX are likely insignificant in the NBH. Biodegradation (de-chlorination), denoted by X, is likely occuring but was not evaluated as part of this study. In model development its rate was assumed to be zero. All mechanisms denoted by a * are important. Although deposition/scour of particles is occuring only a net deposition process was modeled. It appears that Brownian diffusion could be significant but so little is known about the process in bed-sediment that it is not addressed at this time, hence the ? symbol.

In the developments that follow consideration is given to the seperate and joint processes of desorption, molecular diffusion, bioturbation and particle deposition in both the steady-state and transient modes. Transport from sediment to

water is assumed to be the only fate of the PCB. The following is a brief description of each.

Desorption: At this time the PCB molecules are sorbed primarly onto the silt, clay and natural organic matter fraction of the bed sediment. The molecules must physically detach from this sorbent material before they enter the adjacent porewater. This is the desorption process and the molecule is now considered to be "in solution". A molecule is in solution when it is completely surrounded by water molecules. The maximum concentration in solution is the solubility. For Aroclor 1254 at 25°C in seawater this is 12 µg/L and for Aroclor 1242 the value is 88 µg/L. (Dexter and Pavlou, 1978).

Diffusion: Molecular diffusion is a process by which molecules move from regions of high concentration to low concentration through random molecular motions. The process occurs readily in the interstitial spaces between the sediment particles. PCB molecules are transported by this process within and between adjacent pores.

Bioturbation: Sediment processing by animals residing in the upper layers includes burrowing, ingestion/defecation, tube-building and biodeposition. Taken together these processes are termed bioturbation. The net result is the physical vertical and horizontal movement of sediment particles and porewater. PCB molecules either on the particles or in the pore spaces are likewise translocated in the bioturbation process.

Particle Deposition: The Upper Estuary is a net depositional environment (Summerhayes, et al., 1977). Particles enter by the water route under the Coggeshall Street Bridge and settle from the water column onto the bed sediment surface. Over time this results in sediment buildup and a net upward accretion.

These processes taken together affect the transport of PCBs from the sediment to the overlying water. The scenario is hypothesized as follows: Molecules desorb from the particles and are transported by a combination of molecular diffusion and bioturbation. Due to this, they eventually appear at the sediment water interface. Once at the interface, the molecules in solution must move through a water side resistance, attributed to the benthic boundary layer, prior to entering the water proper. The fallout of relatively clean particles onto the sediment surface effectively retards the PCB transport

process for two reasons. The clean particles are mixed downward by the bioturbation process offering fresh sorption sites to the PCB molecules and thereby diluting the concentration in the sediment. Also, the simultaneously slow buildup of the sediment effectively lengthens the transport pathway distance within the sediment.

The particle deposition and bed accretion processes are presently occuring in the Upper Estuary and to a small extent retarding the flux rate of the PCBs. The bioturbation process assures some degree of mixing of fresh particles within the top 2 to 5 centimeters with a lesser degree down to 20 cm. Particles that arrive at the sediment surface are mixed downward so that distinct fresh sediment layers do not form on the surface. Enhancing this ongoing, natural capping process, by mechanically placing a layer (>10 cm.) of clean sediment may shift the bioturbated zone upward away from the PCB contamination, and dramatically reduce the flux rate. Theoretically, capping will change the PCB transport process from one dependent upon relatively rapid bioturbaion processes to the much slower molecular diffusion process.

DEVELOPMENT OF THE CHEMICAL TRANSPORT MODEL

Based on the above review of possible transport mechanisms the concepts controlling chemical transport were established. In this section those concepts will be cast into a quantitative mathematical model from which numerical chemical release rates may be obtained.

The Individual Chemical Transport Processes

There are two general mathematical models for the interpretation and quantification of the effects of bioturbation on the chemical profiles in bed sediment. Berner (1980) describes these as the "box model" approach and the "solid biodiffusion" mathematical treatment. The latter is also refered to as the "conveyor belt" model (Boudreau, 1986). The chemical flux rate equation for biodiffusion of solid particles is:

$$n_A = -D_{A3}^{(t)} d(\rho_B \omega_A)/dy \qquad (1)$$

where n_A is the rate of chemical A in $gA/cm^2 \cdot s$

$D_{A3}^{(t)}$ is the biodiffusion coefficient for the solids in cm^2/s

ρ_B is the bulk density of the bed sediment in g/cm^3

ω_A is the concentration of chemical A on the sediment in gA/g and

y is depth below the interface in cm.

Porewater likely accompanies the solid particles as they are moved by the organisms. An irrigation coefficient is typically used to account for this effect separate from the solids (see Berner).

The "box model" was used early-on in studies of PCB transport in the NBH Upper Estuary but was abandoned when detailed sediment profiles were obtained. An analysis of the consistency between the box model assumptions and the thin layer sediment sample concentration data is presented in the next section.

The PCB Aroclors were modeled as specific chemical species. They are not but it is common to treat these mixtures as such. Dexter and Pavlou (1978) present data on the mass solubilities of the polychlorinated biphenyl in the marine environment. Individual component solubilities of Aroclor 1242 and 1254 in distilled water and artificial seawater are presented. The solubilities of the Aroclors are the sum of the individual component solubilities. In effect these two Aroclors are treated as two specific substances with fixed and constant physical and chemical properties in this report.

These two Aroclors are not very soluble in water. As is shown in a later section the so-called "solubility limit" is often achieved at numerous places within the bed sediment of the Upper Estuary. A detailed discussion of the concept is presented by Thibodeaux (1989) as it applies to the NBH sediments. The solubility limit places a maximum value on the concentration in solution within the porewater adjacent to particles, ρ_{A2}^{**}, mg A/L. The solubility occurs at a chemical concentration on sediment, mgA/kg, of

$$\omega_{AC}=K^{*}_{A32}\rho^{**}_{A2} \qquad (2)$$

where K^{*}_{32} is the equilibrium partition ccefficient, L/kg. The porewater concentration equilibrium curve is therefore divided into two sections. Below ω_{AC} it is assumed to vary linearly with ω_A (i.e., $\rho^{*}_{A2}=\omega_A/K^{*}_{A32}$) and above ω_{AC} it is constant i.e., $\rho^{*}_{A2}=\rho^{**}_{A2}$. The desorption of A-1242 and A-1254 as chemicals species requires adherence to the solubility limit concept.

Molecular diffusion within bed sediment is a slow chemical transport process when compared to the bioturbation process. The slowness of A-1242 moving into lake bed sediment by molecular diffusion was demonstrated recently by Formica et al. (1988). The flux of chemical species in solution due to molecular diffusion is Ficks' first law:

$$n_A=-\mathcal{D}_{A2}\epsilon^{4/3}d\rho_{A2}/dy \qquad (3)$$

where $\mathcal{D}_{A2}$ is the molecular diffusivity of A in water, cm^2/s

ϵ is the bed porosity, cm^3/cm^3 and

ρ_{A2} is the concentration in the bed pore spaces, gA/cm^3.

This equation quantifies the steady state flux rate when the concentration gradient, $d\rho_{A2}/dy$, is constant.

In the case of a long time period transient process for chemical transport, which is the case for PCBs in the Upper Estuary, the following equation applies:

$$\partial\omega_A/\partial t=D_{eff}\partial^2\omega_A/\partial y^2 \qquad (4)$$

where D_{eff} in the case of molecular diffusion is (Formica et al.):

$$D_{eff}=\mathcal{D}_{A2}\epsilon^{4/3}/(\epsilon+\rho_B K^{*}_{A32}) \qquad (5)$$

In this case the transport process of PCBs onto fresh sediment

is dramatically impeded by the presence of fresh sorption sites as reflected by the value of K^{*}_{A32}. This factor is important in retarding the chemical breakthrough time as molecular diffusion occurs through fresh sediment.

The benthic boundary layer on the water side of the interface provides a potential resistance to chemical transport from bed sediment (Boudreau; 1982). This factor is accomodated by a mass-transfer coefficient model. Although the resistance to mass-transport may be small it is none the less included for completeness. The flux rate across this water-side layer is

$$n_A = {}^3k'_{A2}(\rho_{A2i} - \rho_{A2\infty}) \qquad (6)$$

where ${}^3k'_{A2}$ is the m-t coefficient in cm/s,

ρ_{A2i} is the concentration at the sediment-water interface, gA/cm^3 and

$\rho_{A2\infty}$ is the concentration in the water column.

This water side process is in series with the in-bed processes described above.

The fundamental processes described here will be used in the following sections in a more detailed model context to quantify aspects of the present PCB release process and to predict the efficiency of the proposed sediment capping scheme.

Model Analysis of Thin Layer Sediment Samples

Balsam conducted a thin layer sediment sampling program at two sites in the Upper Estuary (Balsam, 1989). The general locations of the two sites are shown on Figure 1. The two were selected to represent different environmental regimes. Station FX was selected because of its proximity to an identified PCB hot spot. Station DR was located in an area believed to be depositional in nature and containing much lower PCB concentrations than the FX site.

Sediment cores from the two sites were sectioned into varying intervals (2-4 cm.) and analyzed for PCBs. The data, in Table No. 1, contains sample designation, the interval from which the sediment layer was collected and the concentration. Chemical analyses were performed on the complete sample sections and account for the PCB both on the solids and in the porewater.

Analysis and interpretation of this data is aided if it is presented graphically as in Figures 5 and 6. The 30.5 cm(12 inch) depth interval average (DIA) concentrations for A-1242/1016 and A-1254 at site FX were 2290 and 760 ppm(wt) respectively. The 30.5 cm DIA concentration for these Aroclors at site DR were 85 and 39 ppm respectively. The following is a detailed interpretation of this data.

The profile at site FX displays high in-bed concentrations with continually decreasing values towards the sediment-water interface. This behavior is characteristic of a site that once received large inputs of PCBs, is now receiving clean sediment, and/or undergoing chemical transport and release of the in-bed PCB content back to the water column. This general shape is qualitative consistent with the box model modified for PCB release to the overlying water column. The modified box model equation is:

$$\ln \omega_A=(1+{}^3k'_{A2}/K^*_{A32}\rho_B\Delta)y/h+C_1 \qquad (7)$$

where Δ is the bed accretion rate, cm/y and C_1 is a constant of integration. Figure 7 contains this transformation of the data at Site FX. The linear behavior in the top 9 cm appears to be consistent with the modified box model for both Aroclors; however the values of h, the completely mixed sediment depth, extracted from the slopes are inconsistent with the profile data. The line slopes in Figure 7 are:

$$\text{slope}=(1+{}^3k'_{A2}/K^*_{A32}\rho_B\Delta)/h \qquad (8)$$

and Table 2 contains the extracted h values for two possible bed accretion rates. These accretion rates result in completely mixed depths of 18 to 59 cm. These depths are inconsistent with the profile data! In the case of A-1242 and A-1254 in Figure 5 the mixed depth appears to be 3 cm at the most. If PCB release to the water column is absent (i.e., ${}^3k'_{A2}=0$) then the completely mixed depth extracted from the modified box model is 5.7 to 8.7 cm. These depths are also inconsistent with the Site FX data plus the no release assumption is invalid. The net result of this analysis is that a modified box model with realistic h values will not fit the data.

The PCB profile at this site suggests that bioturbation processes result in incomplete sediment mixing. However, three of five metal profiles at this same site suggest complete mixing down to a 3 cm. depth. Near constant concentrations with depth is indicative of complete mixing. However, rapid local deposition may give this same result. For transport modeling without deposition it is sufficient to conjecture that rapid mixing is occuring in an upper layer with somewhat slower mixing deeper (ASA, 1989).

The thin profile data at Site DR is more complex and subject to several interpretations. The concentration fluctuations of both Aroclors between 0 and 15 cm depth consist of two high and two low values. Two transport scenarios can be postulated to explain this behavior. One is vertical sediment mixing due to bioturbation and the other is lateral PCB translocation from adjacent source areas.

Allowing that bioturbation is consistent with the significant concentration peaks and valleys, a fairly uniform layer exists down to the 15 cm. level. Bioturbation processes in uncontaminated sediment may mix sediment down to such depths (Whitlatch, 1989). The profiles are consistant with this behavior. If this is true, sites FX and DR are drastically different in bioactivity. The shallow mixing depth at Site FX may be due to depressed bioturbation activity at this highly contaminated site. Areas stressed by pollution may have organism densities 2 to 4 orders of magnitude lower than the normal range (Whitlatch, 1989).

Site DR may be receiving PCB inputs from various source areas in the Upper Estuary and this is the other possible transport scenario. The erratic behavior in the profile suggests that the site has received periodic sediment inputs through bulk transport of sediment from regions of higher PCB content and/or absorption of PCBs from the water column. These high level inputs are interspersed with cleaner sediment inputs.

Another curious aspect of Site DR is that it appears to still be receiving PCBs into the sediment. During the last 15 or more years the average concentration in the top 15 cm. appears nearly constant for both A-1242 and A-1254. If clean sediment is entering the Upper Estuary via the Coggeshall Street Bridge to justify 0.33 to 1 cm./year accretion rate (Teeter, 1988) then a source of PCB must be present to maintain a constant concentration level over the period. This source is

very likely those sediment areas in the upper estuary containing higher levels of PCB contamination than the DR Site.

Due to the failure of the modified box model analysis of the data at Site FX and the lack of a unique explanation for the Site DR data, a biosolids transport model based on less than complete sediment mixing was selected and used in this report. Mixing is occuring in the upper sediment layers but it is not complete mixing. If complete mixing is occuring it is in the top few centimeters (i.e., 1 to 3 cm.) in the highly contaminated areas and possibly deeper in the lowly contaminated areas. Due to incomplete knowledge from location to location, all areas will be treated similarly with a constant biodiffusion coefficient.

It should be noted that for the two Aroclors at both sites FX and DR the 30.5 cm DIA concentration, $\bar{\omega}_A$, is approximately half the maximum concentration over the interval. This fact is important because the 30.5 cm DIA concentration isopleth data in Figures 1, 2 and 3 will be used as the basis for making quantitative PCB release estimates.

A detailed transient mathematical model was constructed and tested against the site FX concentration profile. As noted above, this profile has the characteristic shape for source depletion. It was obtained in a hot spot area and contains the historic record of the cumulative effects of the sediment processes that have occured since 1978. A theoretical transient model analysis was performed that includes the dominant processes of bed accretion, desorption and biodiffusion. The model development and results are presented in Appendix A. The success of the modeling effort is displayed in Figure 1 of that Appendix, where the front portion of the profiles of A-1242 and A-1254 are reproduced by the model using the same values of the accretion rate and slightly different biodiffusion transport coefficients. The values of the latter parameter is within the range of values reported by other investigators for the Upper Estuary (See Table 6). ASA (1989) employs a slightly more complex biosolids diffusion model without deposition and demonstrates success in reproducing the A-1242 profile.

Below the bioturbation zone the process of transport should be primarily molecular diffusion or Brownian diffusion. If this is true, all profiles should display the classical "diffusion tail" of this process as evidence that contamination is moving

further into the bed. Such "diffusion tails" are evident for each Aroclors at both sites from a depth of 15 cm. and deeper (See Figures 5 and 6). A reasonably simple scenario for the creation of such "tails" is as follows.

The discharge of PCB commenced effectively in the mid 1940s and the sediment began to receive these inputs. An active bioturbation zone (~10cm.) resulted in the inputs being incorporated down to this level. Simultaneously, molecular diffusion commenced to transport the PCBs below the 10 cm. level and the process has continued to this day. If the in-bed concentration at the y=15 cm. level is assumed constant for the past 42 years the semi-infinite slab model may be used to interpret the profile data. Formica et al. (1988) presented this model and a similar analysis of lab data.

In the face of uncertain information regarding the discharge history and events occuring in the overlying water column above a particular site the most robust model is one that makes minimum assumptions about these events. The semi-infinite slab model is one such robust model. It requires a constant source concentration and the diffusion time. This model was used in the analysis of the data in that portion of the profiles between 15 and 38 cm. and the diffusivities, extracted according to Formica, et al. (1988), appear in Table 7. The diffusion time was 42 years.

The values of the effective retarded diffusion coefficients $\mathfrak{D}_{A3}$, for the two Aroclors at each site are very similar. This implies that a consistent transport mechanism is operative at depths of 15 cm. and beyond. The two locations in the Upper Esturary are separated by a distance of 820 meters (2700 ft.). Three of the data sets display $\mathfrak{D}_{A3}$ values of 6.8E-9, 5.4E-9 and 4.6E-9 $cm.^2/s$ respectively. These are in the range of laboratory derived values reported by Formica et al. (1988) for A-1242 diffusing into lake bed-sediment. The $\mathfrak{D}_{A3}$ values for A-1254 at Site FX are two to three times higher than the others. The profile at this Site does not have the classical shape throughout the interval as can be seen in Figure 5. The reason for this unusual shape is unknown and likely responsible for the elevated $\mathfrak{D}_{A3}$ values.

Using Equation 5 it is possible to estimate the effective sorption coefficient representd by the above effective retarded diffusion coefficients, $\mathfrak{D}_{eff}$. Molecular diffusivities are from

Table 12. For a porosity of 50% and bulk density of 0.75 g/cm^3 the effective sorption coefficients are 350 and 451 L/kg for A-1242 and 161 and 552 L/kg for A-1254.

An average effective retarded diffusion coefficient, based on the three consistent sets, is 5.6E-9 cm.^{2}/s or 0.18 cm.^{2}/y. These values are approximately fifty times lower than the raw bioturbation values, $\mathfrak{D}_{A3}^{(t)}$=10 cm.^{2}/y, in Table 6. Since the $\mathfrak{D}_{A3}^{(t)}$ are particle transport values the effective chemical turbulent diffusivities are $\mathfrak{D}_{A3}^{(t)}\rho_B K^*_{A32}$. For the respective partition coefficients they are 59,400 cm.^{2}/y for A-1242 and 161,700 cm.^{2}/y for A-1254. So in reality the bioturbation driven chemical transport process in the top 10 cm. is 300,000 to 900,000 times more rapid than the molecular driven process at the 15+ cm. depth when both are placed on a chemical porewater concentration gradient basis. This fact suggests that relocating PCB contaminated sediment deeper below the actively bioturbed zone should dramatically reduce the emission rate to the water. The relocation, besides lengthening the diffusion path, forces the chemical transport process to change from a rapid particle mechanism to the much slower molecular mechanism.

The Steady State Flux Model

The model analysis studies performed in the previous section indicate that the transport process, the concentrations levels and the flux rates change very slowly with time. For example, the profile shown in Figure 5 is the result of in-bed processes that have been occuring for as long as forty years. This being the case, concentration profile data may be used with steady state flux equations to obtain rates that are constant for short time periods. For example, it is reasonable, in the case of the Upper Estuary, to use field measured profile data obtained about Jan. 1, 1989 with the steady state flux for estimates of release rates that are reasonably accurate for two to three months on either side. This is the basic assumption that underlies the steady state flux model developed in this section.

Figure 8 illustrates the three zones in the bed sediment region that regulate the chemical release process. On the water side just above the interface is the benthic boundary layer. This layer is generally characterized as one containing

very slow moving water (Boudreau and Guinasso, 1982). Immediately below is the layer of bioturbation and beyond is the molecular diffusion layer. A hypothetical concentration profile for PCBs is shown in Figure 8. The transport within the bioturbation zone requires some mechanism analysis and model development before it can be applied.

As presented previously, the life maintaining activities of the organisms in this zone move particles and porewater (Aller, 1982). The characteristic "conveyor belt" velocity can be scaled by $\mathbb{D}_{A3}^{(t)}/\Delta y$, where Δy is the vertical distance over which particle and water movement occurs. From depth y_b (in Figure 8) the particles are moved physically to the interface (y=o) and are eventually returned to y_b. They lose a fraction of their PCB content when at the interface. Therefore, at steady state the rate of chemical movement through the zone is the sum of the particle and water contributions:

$$n_A=\frac{\mathbb{D}_{A3}^{(t)}\rho_B}{y_b-o}(\omega_{Ab}-\omega_{Ai})+\frac{\mathbb{D}_{A2}^{(t)}\epsilon}{(y_b-o)}\ (\rho^*_{A2b}-\rho^*_{A2i}) \qquad (9)$$

where the subscripts b and i denote the limits of the bioturbated depth and the sediment-water interface. Whitlatch (1989) suggests that $\mathbb{D}_{A3}^{(t)}=10\mathbb{D}_{A3}^{(t)}$. Equilibrium is assumed to exist between particle and pore water at all points along the concentration profile. This is a reasonable assumption considering the slowness of the in-bed processes. With these assumptions Equation 9 can be simplified to:

$$n_A=\frac{\mathbb{D}_{A3}^{(t)}\rho_B}{y_b}(\omega_{Ab}-\omega_{Ai})\left[1+10\epsilon/\rho_B K^*_{A32}\right] \qquad (10)$$

For A-1242 and A-1254 the numerical value of K^*_{A32} are so large that the bracket term is very nearly unity.

At steady-state there are three possible resistances in series when taken together control the rate of chemical transport from the bed sediment. Equation 10 describes only one. Accounting for all three yields the flux equation:

$$n_A = {}^2K'_{A3}(\rho^*_{A2} - \rho_{A2}) \qquad (11)$$

where ρ^*_{A2} is the porewater concentration in equilibrium with the chemical concentration in sediment of ω_A and

$$1/{}^2K'_{A3} = 1/{}^3k'_{A2} + y_b/\mathfrak{D}^{(t)}_{A3}\rho_B K^*_{A32} + (y-y_b)/D_{A3} \qquad (12)$$

where $y>y_b$ is the depth molecular diffusion commences and the value of ω_A measured. The development of this latter equation originates from a simple difference relationship of the porewater concentrations at points y_m, y_b, y_i and in the overlying water column. This equation will be used as the basis for the steady state flux calculations. Its use assumes a concentration profile with a negative slope as depicted in Figure 8.

Chemical solubility places some limitations on the range of ρ^*_{A2} values that are valid for use in Equation 11 and on the parts of the rhs of Equation 12 that need be included. The numerical value of ω_A, the high end of the concentration profile, in relation to ω_{AC} is used to determine the above limitations. In the case of the Upper Estuary ω_{AC}=260 ppm for A-1254 and ω_{AC}= 640 ppm for A-1242. At these values the porewater contains the Aroclors at the solubility limit. If $\omega_A<\omega_{AC}$ at all points on the profile and $y=[y_b, y_m]$ then Equations 11 and 12 apply as written. The exact location of y, or the thickness of the molecular diffusion layer is difficult to determine. If $\omega_A \geq \omega_{AC}$ on $y=[y_b, y_m]$ then $\rho_{A2} = \rho^*_{A2}$ in Equation 11 and the last term on the rhs Equation 12 is dropped. In this latter case the porewater beyond $y=y_b$ is saturated and therefore constant implying no gradient for molecular diffusion. Transport by bioturbation is not so limited since it is a particle driven process and not subject to the thermodynamic limitation of solubility.

If $\omega_A>\omega_{AC}$ on $y=[o, y_b]$ the last term in Equation 12 disappears again and is combined with Equation 11 to take the form:

$$n_A = \rho_B(\omega_A - \omega^*_A)/[\rho_B K^*_{A32}/{}^3k'_{A2} + y_b/\mathfrak{D}^{(t)}_{A3}] \qquad (13)$$

Here ω_A is measured at y_B and the concentration difference appears in terms of sediment rather than aqueous solution. This allows the use of concentration gradients which exceed the solubility limit, which is the proper form when bioturbation is present.

As a special case it should be noted that if ω_{Ai} is known with certainty then only the first term on the rhs of Equation 12 need be used. A simple steady state flux rate equation is applicable and it is:

$$n_A = {}^3k'_{A2}(\rho^*_{A2i} - \rho_{A2}) \qquad (14)$$

ASA (1987) used this approach in estimating the flux from the Upper Estuary. The numerical values of the flux are sensitive to the $\omega_{Ai}(=\rho^*_{A2i}K^*_{A32})$ values and the latter are hard to measure with certainty. Only through thin layer sediment sectioning is it possible to estimate ω_{Ai} with any degree of certainty. This has been performed only at sites FX and DR.

The final working equation for computing the sediment flux is:

$$n_A = \rho_B(2\bar{\omega}_A - \bar{\rho}_{A2}K^*_{A32})/\left[\rho_B K^*_{A32}/{}^3k'_{A2} + y_b/\mathfrak{D}^{(t)}_{A3}\right] \qquad (15)$$

where $\bar{\omega}_A$ is the 30 1/2 cm DIA PCB concentration on sediment and $\bar{\rho}_{A2}$ is the PCB concentration in solution for the water column. The effective high end of the concentration gradient is approximated as twice the DIA value. This factor has a basis in mass-transfer theory and also in fact. Evidence for the latter is in the thin layer data at both sites FX and DR. Also an implicit assumption made when Equation 15 is that $\omega_A = 2\bar{\omega}_A$ occurs at $y=y_b$. The depth where the maximum concentration occurs and its numerical value are obscured when sediments are mixed over large depth intervals prior to analysis. This is one of the major faults of trying to estimate flux rates based on field data averaged on depths of 30 1/2 cm. (12 inches). Despite these uncertainties, Equation 15 is the best choice for

estimation of the flux rate of PCB from sediment to water at this time.

SELECTION OF DATA

The data used in all numerical calculations in this report are presented in this section and their origin specified and/or described.

Time of Important Events

The transient nature of the PCB processes in the Upper Estuary is an important factor in building a comprehensive transport model. Time is an independent variable and appears explicity in the transient model equations. Four benchmark dates are important and have been assigned as follows:

1947 - the discharge of PCBs to the Upper Estuary commenced,
1978 - the discharge of PCBs to the Upper Estuary had virtually stopped,
1985-86 - sediment PCB samples were obtained by others (Condike, 1986), and
1988 - the thin layer sediment samples were obtained by Balsam.

It is difficult to be absolutely sure about the 1978 event so this date is interpreted to mean that discharge "effectively" ceased in that year. The discharges may not have abruptly stop in 1978 but nevertheless twelve years is used as the lapsed time in the transient model analysis (see Appendix A).

Isopleths of PCB Concentrations in Bed Sediment

Balsam Environmental Consultants, Inc. (Balsam) prepared four figures depicting PCB concentration isopleths for the Upper Estuary. These include the combined A-1016/1242, A-1248, A-1254 and total PCBs. This isopeth data is shown in Figures 1 through 4. From these figures the fraction sediment surface areas (of the Upper Estuary) between adjacent concentration isopleths were determined. The tabulation of this data appears in Table 3.

PCB Concentrations in the Water Column

The water column above the bed sediment receives the PCB originating from the bed sediment. Equation 15 contains the variable and displays how it effects the PCB release rate from

the sediment. In this equation if $\bar{\rho}_{A2}K^{*}_{A32}>2\bar{\upsilon}_{A}$ the particular area is sorbing PCBs from the water column.

Teeter (1988) reported on measurements of total PCB concentration and total suspended material at the Coggeshall Street Bridge from samples taken in 1986 and 1983. Balsam (1987) prepared a report based on the Batelle water column sampling data. This data was reviewed. With a simple particle/water equilibrium model (Thibodeaux, 1989) it was determined that 76% to 90% of the total PCBs in the Upper Estuary water were in solution. Based on this data and assuming 70% was A-1242 and 30% was A-1254, the in-solution average values are 1.1 μg/L A-1242 and 0.5 μg/L A-1254. The 70% vs 30% split of the two primary aroclors was arrived at from an analysis of the U.S. Army COE-Condike report (1986). From this report it was also determined that the sediment column contained 4% organic matter.

Physicochemical Properties

The U. S. Environmental Protection Agency published values of key chemical properties for the priority pollutants and these were used as a basis. These data appear in Table 4. The values of K_{oc} and water solubility are for freshwater at 25°C. Both K_{oc} and solubility are effected by the salts in the marine water. Corrections were made using the Setschenow equation. The constant reported by Baron (1988) was used for K_{oc} and the data on Aroclor solubilities presented by Dexter and Pavlou (1978) was used for the determining the Setschenow constant for marine waters. The corrected values appear in Table 5. The partition coefficients in this table reflect the 4% organic matter content of the bed sediment (Condike, 1986).

Bio-diffusion Coefficients for Bed Sediment

The mathematical analysis performed on the thin layer sediment samples at site FX in the Upper Estuary yielded the most current and realistic biodiffusion coefficients (Appendix A). The values were 3.36 cm^2/y for Aroclor 1242/1016 and 7.1 cm^2/y for Aroclor 1254. These values and those extracted from other sources appear in Table 6. Based on this data a value of 10 cm^2/y was chosen for calculation purposes. The effective variation in $\mathbb{D}_{A3}$ is approximately ± 7 cm^2/y.

Whitlatch (1989) summarized the biological activities of

burrowing aquatic organisms and reviewed penetration depths and sediment re-working rates. Myers (1977) performed laboratory studies of infauna sediment processing. Average sediment turnover times, τ_i, in the top 1 cm, 2 cm and 10 cm (h_i values) were combined in a resistance-in-series fashion over the total depth, h_t=10 cm., to compute crude $\mathcal{D}_{A3}^{(t)}$ values from the relationship: $h_t/\sum(\tau_i/\Delta h_i)$. These crude values fell within a range of 39 to 170 cm^2/y. Although this study does provide evidence of a direct link between sediment turnover times and $\mathcal{D}_{A3}^{(t)}$, the range of the laboratory values were beyond those reported by others (see Table 6) for the New Bedford Harbor region and therefore not considered further in this work.

Other Data

The following list summarized the other data and sources:

Tidal water exchange per cycle 0.92E9L in the upper Estuary (Balsam).

PCB evaporation mass transfer coefficient, K_e=7.0cm/h (Thibodeaux, 1989).

Tidal current speed (7.5 cm/s), water column depth (91.4 cm), and procedure for computing benthic boundary layer mass-transfer coefficient (2.1 cm/h) was obtained from Spaulding (1987).

Sediment deposition rates (1.0 cm/y) were determined from the Condike (1986) report and (3 mm/y) from Teeter (1988).

Dry bulk density of Upper Estuary sediment is 0.75 g/cm^3 and particle density of 2.3 g/cm^3 (Balsam). The sediment surface area is 7.69E9 cm^2(190 acres).

CALCULATED SEDIMENT BED RELEASE RATES

The observed thin layer concentration profile at site FX was the result of PCB out migration, biodiffusion plus the deposition of clean sediment on the sediment-water interface (Appendix A). The peak concentration observed at the site was assumed to be the uniform initial concentration in 1978 when PCB discharge effectively ceased. The governing equation is transient and an analytical solution was obtained. One

adjustable parameter, $\mathfrak{D}_{A3}^{(t)}$, was used to calibrate the model. This aspect was presented in a previous section. Once calibrated to the site FX concentration profile data the model equation was transformed to yield the flux rate at the sediment water interface. This flux equation is transient (Equation 9 in Appendix A) and capable of yielding PCB release rates during any year after 1978. The rates for January 1989 at site FX are presented in Table 8. This model is the most mathematically sophisticated of those used in this study in that it contains both time and space information.

It was argued in a previous section that the transient process is slow and recent concentration profile measurements, such as for sites FX and DR, can be used with steady-state flux models to estimate current PCB emission rates. Equation 15 is one such equation which used the 30₁/₂ cm DIA concentration to estimate the flux. Equation 14 is another but it employs the PCB concentration at the sediment-water interface. Both were used to estimate the present release rates at sites FX and DR. The results appear in Table 8.

A review of these results indicate generally good agreement agreement among the three models for the flux rate of both Aroclors. The three radically different modeling approaches yield comparable rates. Although the same transport processes are imbedded in the models, the concentration gradients used are different. The concentration profile at site FX is ideal for this type of analysis. The data at site DR is not so ideal. It was so un-characteristic of a diffusion-type profile that a transient model fit was not attempted. The flux rate based on the interface concentration and used in Equation 14 is likely the most reliable estimate of the flux at the DR site. However, for this complex profile the use of a 30₁/₂ cm. DIA concentration in Equation 15 yields only a rough approximation of the true rate.

The 30₁/₂ cm DIA concentrations presented for A-1242, A-1248 and A-1254 in Figures 1, 2 and 3 were used as the basis for estimating emission rates from the sediment to the water column. Equation 14 was the one employed for the flux calculation. The $\bar{c}_A$ values were those mid-way between the concentration of adjacent isopleths. These concentrations and the associated fractional areas of the Upper Estuary are shown in Table 3. The emission rates are a product of the flux, n_A,

the fractional total area (190 acres). The calculation yields the annual emission rate in kg/y. The mid-range concentrations and the emission rates for each of the three primary Aroclors appear in Table 9. The rates represent the years 1985 and 1986 when the data for for $\bar{\omega}_A$ was obtained.

The release rates to one significant figure are 6000, 400 and 2000 kg/y for A-1242, A-1248 and A-1254 respectively. The total of the three is 8400 kg/y. These individual Aroclor values represent 71%, 5% and 24% of the total. Table 10 summarizes the totals by concentration isopleth range and fractional area occupied. The total emission rates are the sum of the three Aroclors. The fractional areas result from Figure 4. In this figure the total PCB concentration represent the three primary Aroclors and PCBs altered by the natural or anthropogenic processes.

The negative rate values that are the first entries in both Tables 9 and 10 represent areas of the Upper Estuary where PCB are being adsorbed onto the bed sediment from the water column. This involves about 15% of the surface area and comes about mathematically because $\bar{\rho}_{A2}K^{*}_{A32} > 2\bar{\omega}_A$ in Equation 15. This undoubtly occurs in fact because the source areas are releasing the PCB at high concentration levels and as this water flows over the cleaner areas the PCBs re-adsorb.

The total PCB emission rates and fractional areas in Table 10 are presented along with various derivatives of this basic data. Columns three and six represent cumulative percent areas and cumulative percent emission rates respectively. The addition commences with the most highly contaminated areas and is summed upward. Column three originates from column two and six from five.

Graphical displays of the emission rates allow a clearer interpretation of the results. Figure 9 displays the cumulative release as a function of concentration in the sediment. The abscissa in this figure commences with the highest concentration sediment sources. It shows that only 30% of the PCBs originate from sediment contaminated at 5000 ppm or higher. Using sediment surface area as the independent variable also allows a realistic interpretation of the results. Figure 10 is such a display. The cumulative % area commences with the hot spots of 20,000 ppm and moves to the less concentrated spots. This figure shows that nearly 80% of the emissions occur from 30% of

the Upper Estuary bottom sediment. Also 97% of the emissions occur from 60% of the sediment area. Figure 11 shows the incremental % release with the same abscissa variable. Large incremental release rates are involved in the hot spot areas of 2000 to 10,000 ppm and in the 100 to 500 ppm area. The former is due to the high concentration of these spots and latter is due to the large surface area occupied by these spots. The area between the 100-500 ppm isopleths accounts for nearly 30% of the Upper Estuary sediment surface.

ERROR ANALYSIS OF THE RELEASE RATE

A brief review of the "Selection of the Data" section will reveal that some key parameters used in the flux rate calculation display a large range of variability. The choice of average values from this range implies a degree of uncertainty in the calculated fluxes. In this section a formal error analysis procedure will be used to establish an interval of maximum likelihood for the PCB flux from the Upper Estuary.

The release rate of PCBs is estimated using Equation 15. In this equation the dominant part is that contributed by the bioturbation process:

$$W_A \tilde{-} \mathfrak{D}_{A3}^{(t)} \rho_B f_A A 2\bar{\omega}_A / y_b \qquad (16)$$

where the product $f_A A$ is the sediment surface area between adjoining isopleths. Table 11 contains the average values, uncertainty intervals and relative errors of the three primary parts of Equation 16. The second entry in the last column reflects the uncertainty in the PCB concentration for the 30½ cm DIA. Since the other parameters in this group are known with certainty, the ±5% reflects the uncertainty in the chemical analysis of the PCBs. The other uncertainty intervals are based on the data in Table 6.

Performing a formal mathematical error analysis on the three parts of Equation (16) yields the following relationship for the relative error of the emission rate:

$$\left[\frac{\Delta W_A}{W_A}\right]^2 \tilde{-} \left[\frac{\Delta \mathfrak{D}_{A3}^{(t)}}{\mathfrak{D}_{A3}^{(t)}}\right]^2 + \left[\frac{\Delta(\rho_B f_A A 2\bar{\omega}_A)}{\rho_B f_A A 2\bar{\omega}_A}\right]^2 + \left[\frac{\Delta y_b}{\bar{y}_b}\right]^2 \qquad (17)$$

where the rhs are the three relative error terms quantified in Table 11. The relative error in the emission rate is therefore

$$\Delta W_A/W_A=\left[(6/10)^2+(1/20)^2+(5/10)^2\right]^{1/2}=0.78$$

Based on this value the interval of maximum likelihood for the PCB flux rate is

$$W_A=\bar{W}_A\pm\Delta W_A=\bar{W}_A(1\pm0.8) \qquad (18)$$

where $\bar{W}_A$ is the emission rate based on the average (or mid-range) values of the three primary parts. Table 11 contains the calculated results for total PCBs. This same interval applies to the flux rate values reported in Table 9 for the individual Aroclors.

The interval of maximum likelihood for the total PCBs being emitted from the sediment to the water column is large. Using two significant figures it ranges from 1700 to 16,000 kg/y. Based on a different modeling approach and the work of other investigators, an independent evaluation of the reasonableness of this interval is presented in the following sections.

OVERALL MASS BALANCE AND FATE ANALYSIS MODEL

In this section the overall consequence of the PCB release for the water and air media associated with the Upper Estuary will be considered. If the rate of PCB degradation by chemical or biological reactions is presumed very slow, the primary outward pathways for movement of the sediment bed originating PCBs is by water under the Coggeshall Street Bridge and evaporation from the water surface to the air. Figure 12 illustrates the primary PCB pathways from the Upper Estuary. In this figure "a" denotes the release from the sediment, "b" the evaporation to air, "c" the flow under the Coggeshall Street Bridge and "d" the flow out into Buzzards Bay through the Hurricane Barrier.

The conceptual pathway diagram for PCBs in the New Bedford Harbor consist of two compartments. The Upper Estuary box is of

primary interest. This box contains the major amount of PCBs and all the significant pathways are considered. The small inflow from the Achusnet River is ignored. The tidal driven flows, pathway "c", is the dominant water exchange and flushing process in the Upper Estuary. The Lower Estuary processes are of secondary interest but are included in a very crude fashion to acknowledge that its waters are not PCB free. In this regard all the processes occuring with respect to PCB in the Lower Estuary, that include absorption/desorption, evaporation and advection, are assumed to occur cumulatively and be effectively accounted for by pathway "d".

Overall PCB mass balances at steady-state were performed on box-1 and box-2 in Figure 12. The resulting equations were solved simultaneously for the concentration in box-1 or under the Coggeshall Street Bridge. The relationship is:

$$\rho_{A2}=\frac{W_A+\rho_{A2B}Q_uQ_L/(Q_u+Q_L)}{Q_u+AK_e-Q_u^2/(Q_u+Q_L)} \qquad (19)$$

where ρ_{A2} is the PCB concentration in the Upper Estuary, g/cm^3

W_A is the sediment bed release rate, g/y

ρ_{A2B} is the concentration in Buzzards Bay, g/cm^3

Q_u is the annual water flushing rate of the Upper Estuary, cm^3/y

Q_L is the rate for the Lower Estuary, cm^3/y

A is the water surface area of the Upper Estuary, cm^2 and

K_e is the PCB evaporation coefficient for the Upper Estuary, cm/y

Calculations were performed with Equation 19. The primary variables of interest are the concentration, ρ_{A2}, and the emission rate, W_A, in the Upper Estuary. Q_u was obtained assuming two tidal cycles per day. Q_L was chosen to be five times Q_u. This means the water flow rate through the Hurricane Barrier is 5 times greater than that at the Coggeshall Street Bridge. The surface area and evaporation coefficient are in the data section.

Graphical solution results of Equation 19 are presented in Figure 13. The two dashed lines assume no evaporative loss of PCB. The two solid lines assume evaporative losses. The two quantities Q_u and AK_e in Equation 19 account for the water route and evaporation route losses of PCBs respectively. Therefore, the percent evaporated is:

$$\% \text{ Evaporated} = 100\ AK_e/(Q_u + AK_e) = 41\%$$

for $Q_u = 1.84E6 m^3/d$, $A = 7.69E5 m^2$ and $K_e = 1.68$ m/d. The other 59% of the PCBs exit by the water route under the Coggeshall Street Bridge. The results of two PCB concentration levels, 0.0 and 100 ng/L, at the Hurricane Barrier are represented in Figure 13. There are two sets of curves, one set with evaporation and one without. In each set the upper one is for 100 ng/L and the lower is 0.0 ng/L. ASA (1989) performed an independent assessment of the evaporative losses and arrived at a coefficient of $K_e = 2.37$ m/d. Based on this coefficient, the evaporative loss of PCB from the upper estuary was placed at 50%.

Evaporation of PCBs from water has been established in theory (Thibodeaux, 1979) in the laboratory (Shen and Tofflemire, 1980) and in the field (Larsson, 1985). The no-evaporation curves are included only to indicate the significance of evaporation. The dotted line that commences with a ρ_{A2} value on the ordinate, proceeds to the evaporation line and then downward to a ω_A value on the abscissa, represents a valid PCB mass balance. (ASA 1989)

The lines, both dashed and solid, in Figure 13 represent the conservation of mass in the Upper Estuary. In this case it is for the total PCBs originating from the bottom sediment, W_A. If a certain amount is released from the sediment then a steady state concentration, ρ_{A2}, should be manifest in the water, provided mass is conserved. The equation (No. 19) or its graph (Figure 13) must work in the reverse also. If a concentration in water is measured this implies a certain release rate. Fine tuning the mass balance is done by considering or not considering evaporation and the "background" PCB concentration in Buzzard's Bay. These parameters are also indicated on the

figure.

ASA (1989) reviewed and summarized data sets obtained by various investigators that is included in reports issued by EPA, Battelle, and the Waterways Experiment Station. In this summary the total PCB concentration in the water column of the upper estuary ranged from 500 to 5000 ng/L. This range of concentrations, ρ_{A2}, is shown on the ordinate of Figure 13. A corresponding range of release rates, ω_A, from the bed sediment is indicated on the abscissa of Figure 13. The range, set by using the evaporation lines, varies from 500 to 6000 kg/y.

WATER FLOW-BY-CONCENTRATION MODEL

The point mass flow rate of a chemical moving through an imaginary plane surface (area ΔA^i) can be estimated by simultaneous water velocity (v^i) and concentration (ρ^i_{A2}) measurements at the plane. The velocity determinations, both positive and negative, are perpendicular to the plane. Integration of the point flux valves, $v^i\rho^i_{A2}$, over the entire plane surface yields the net rate

$$W^P_A = \sum_{i=1}^{n} v^i \rho^i_{A2} \Delta A^i$$

in mass per unit time (i.e., kg/y). As the total number of point measurements (n) goes to infinity ($n\rightarrow\infty$) over a very short sampling (sample time$\rightarrow$0) this water flow-by-concentration model gives the exact rate assuming the velocity and concentration measurements are exact (i.e., precise and accurate).

This so-called direct measurement technique is in reality a model because both the point flux determinations and the sample time must be finite numbers. In other words the investigator must make a choice of how many samples (velocity and concentration) and how long to sample (time period). Since these will not be infinite and zero respectively the basic assumption of the model has been violated. Never-the-less this model is generally accepted as a direct measurement technique with attention to a proper choice of the number of samples and the sample time.

A significant fraction of the PCBs released from the

sediment in the upper estuary can be estimated by the water flow-by-concentration model technique. In this case planes are choosen at the Coggeshall Street Bridge and Achusnet River inlet. As illustrated in the upper estuary box-1 of Figure 12, this technique can theoretically measure the rate at point c. However, the rate at point b, evaporation, must be accounted for.

Several determinations of the horizontal flux of PCBs through the Coggeshell Street Bridge transect has been made by EPA, WES and ASA. This measurement employed the water flow-by-concentration model in intensive tidal cycle surveys. These measurements were summarized and critiqued by ASA (1989). A total of twelve measurements were reported. The individual values, multiplied by 2 to account for evaporation, appear in the next to last column of Table 15. The values range from 100 to 3300 kg/y.

This model and the previous estuary mass balance model is based on water column data. The range in the emission rates are due primarily to the variations in the measured PCB concentrations in water and the measured tidal cycle velocities. The emission rate range was 500 to 6000 kg/y for the estuary mass balance model and 100 to 3300 kg/y for the water flow-by-concentration model.

Both models contain a parameter that quantifies the PCB lost by evaporation to air. This parameter, the coefficient K_e, is in Eq. 19 of the estuary mass balance model. The water flow-by-concentration model PCB rate, W_A^P, is modified for evaporation losses to yield

$$W_A = W_A^P(1+K_eA/Q_u)$$

where W_A is the PCB rate from the sediment. The primary variable that effects the magnitude of K_e is the wind velocity. Lunney et al. (1985) demonstrated that this coefficient increases with the square of the wind velocity. Table 16 contains values of K_e as a function of wind velocities. The wind velocity range in the table has been observed in the New Bedford Harbor area (ASA, 1989).

The evaporation component is a significant fraction in the water column models for PCB rates. The correction factors in

the above equation appear in the last column of Table 16. It ranges from 1.7 to 4.8. The values used in the PCB rate presented in Table 15 were 2.0 and 4.8. These rates appear in the last two columns of that table. Complimentary parameters illustrating the importance of evaporation also appear in Table 16. Column three is the percent PCB mass rate from the sediment lost to air. For a 20m/s wind this factor is 79%. Column four contains the theoretical PCB evaporation half-life in hours. A water column depth of 91.4 cm was used in this computation. The relative short evaporation half-life values indicates the speed of evaporation.

SUMMARY OF MODEL PREDICTION

Details of three separate chemodynamic models for estimating the PCB leaving the bed sediment of the upper estuary were presented above. These models were: a bed sediment transport model, an overall estuary mass balance model and a water flow-by-concentration model. Figure 14 is a graphical logarithimic number line summary of the results of all three models. The sediment-side model appears above the line. Both water-side models appear below the line. The ranges of the annual PCB rate in kg/y are indicated for each model. There is a common region of overlaping rates for the three models. This region is from 1700 kg/y to 3300 kg/y.

A semi-quantitative scheme was developed to provide a common basis for comparing, on a relative scale, the degree of confidence inherent in the three models. This scheme boils down to questions of certainty about key parameters in the model equations. The question is; how certain is one in the choice of this parameter (or parameters) for the upper estuary? The mean annual tidal water exchange volume between the upper and lower estuary was defined to be a known with good certainty. The choices are good, average and poor. Table 17 contains the results of the comparison scheme.

The concentrations measurements of PCB in the water column are abundant in number and of "good" confidence. The same is true of the PCB concentrations in sediment. The number of velocity·concentration·area measurements at the Coggeshall Street Bridge are not so abundant. Two parameters (ν^i and ρ^i_{A2}) are involved as a product and this certainty was judged average to good. The evaporation coefficient is known with "average"

certainty. Due to these factors, the certainty of estuary mass balance madel is judged the (slightly) superior of the two water-side models. Even though the evaporation parameter is known with average certainty, its value is likely to be higher than that used to arrive at the results in Figure 14 Based on the wind velocity data it is not likely to be lower than 1.68 m/d. This uncertainty analysis of K_e causes the ranges in the PCB rates for both water-side models to be shifted to higher values. Based on the fraction evaporated numbers, E, in Table 16, the shift increases the indicated values below the line in Figure 14 by a factor of 2.1. The high-end rate values are shown in the fifth column of Table 15.

The selection with certainty of any single values of the bioturbation coefficient and depth for characterizing the upper estuary sediment condition is poor. A range of values of these two parameters entered into an uncertainty analysis that produced the 1700 to 16,000 kg/y PCB rate range shown in Figure 14. The high end of this range reflects high numbers of active organisms. It is likely that the pollutant level in the bed sediment is inconsistent with the high numbers of active organisms represented by the bioturbation coefficients for clean sediment. The high end of this range, 9000 to 16,000 kg/y, is possibly unrealistic. The low bioturbation coefficients used in the uncertainty analysis are likely characteristic of polluted sediment and the lower end of the rate range, 1700 to 9000 kg/y, is possible quite realistic.

Based on the above discussion and the range of coincidence of predictions from the three models the rate of PCB leaving the sediment is most probably in the range of 500 to 6000 kg/y.

PART III: PCB TRANSPORT THROUGH CLEAN CAP MATERIAL

This section of the report contains the theoretical results on the effectiveness of capping the contaminated bed sediment of the Upper Estuary with clean sediment to reduce PCB emissions to the water column. The order of presentation will include a review of laboratory tests on capping effectiveness, theoretical transport models for PCB migration through caps, and finally estimated release rates.

LABORATORY TESTS AND RESULTS OF CAPPING EXPERIMENTS

Brannon et al. (1985) have developed an experimental methodology for testing the effectiveness of capping in isolating contaminated dredged material from biota and the overlaying water. The procedure uses both large (250 L.) and small (23 L.) laboratory scale reactor units, non-absorbing chemicals such as oxygen (O_2), ammonia-nitrogen (NH_4-N) and orthophosphate-phorphorus (Ortho-P) in 40 day steady-state experiments to compare the effectiveness of cap thicknesses ranging from 5 cm to 50 cm. Three capping materials, sand, clay and silt, were evaluated for their efficiency in preventing transfer of contaminants from a bed sediment into the overlying water column and biota. They reported that a thick cap (50 cm or more) of any of the materials tested effectively isolated the overlying water and non-burrowing biota from the contaminated sediment.

Sturgis and Gunnison (1988) performed laboratory tests using the Brannon et al. methodology on capping meterial thichnesses that would chemically isolate New Bedford Harbor sediments from the overlying water column and biota. The small scale test units were used and the rationale was that a cap thichkess that is effective in preventing the movement of the soluble tracers NH_4-N and Ortho-P will also be effective in preventing the movement of PCBs that are strongly absorbed by sediment. The test period was thirty days. The results were that a cap 35 cm. in thickness, which was effective in preventing the release of NH_4-N and Ortho-P, would also be effective in preventing the movement of PCBs into the overlying water column. In general they recommended a 55 cm cap for the New Bedford Harbor sediment with the caveat that if a specific deep burrowing organism is present the cap be extended to 445 cm.

The above two works were aimed at the steady-state chemical release rates with capping. The results inferred for PCBs based on the results of the tracer chemicals is true but not for reason given. Theoretically, the high absorption property of PCBs onto sediment plays a significant role in retarding transport during the transient period prior to breakthrough. After breakthrough

and when steady-state transport has been achieved the sediment cap is at its sorptive capacity with respect to PCBs. At this time the same quantity that enters the cap through the bottom surface leaves through the upper surface. This very advantageous property of the PCBs, in comparison to the test chemicals used by Sturgis and Gunnison, was not tested. The breakthrough times for NH_4-N and Ortho-P are a few weeks. For example, with a 15 cm. cap the theoretical breakthrough time is 26 days. The slow transient nature of Aroclor-1242 in lake bed sediment was reported by Formica et al. (1988). In 64 days the substance moved less than 1 cm. into the sediment bed. At the end of 128 days the substance was not detected at a 1.5 cm. depth. These lake bed experiments were conducted without bioturbation process present. The tanalysis of the "diffusion tails" of the thin layer presented on p. 10 and 11 support the slow movement of PCBs below the bioturbed zone in New Bedford Harbor sediment. The "tails" displayed in Figures 5 and 6 beyond the 15 cm. depth show that the Aroclors moved downward approximately 15 cm. in 42 years.

It is clear from the above that some laboratory and field data exists to support capping with clean sediments. Theoretical models have been proposed (Formica, et al., 1988) that may be used for predictive calculations of chemical breakthrough times and flux rates through the cap. The next section contains such a presentation.

THEORETICAL MODELS FOR PCB MIGRATION THROUGH SEDIMENT CAP MATERIALS

The theoretical model concepts that apply in the cap are identical to those that apply in the original contaminated bed sediment. These concepts which include both the transport mechanisms and the transport models, appear on pages 4 to 7. The models also apply to both the transient and steady-state processes. Figure 15 contains one illustration of the original sediment (a) and the capped sediment (b).

Prior to applying these models it is important to present some factors about the entire capping process so that the predictions can be evaluated in the proper context. These factors include cap placement, consolidation of sediment, organism recolonization, bed accretion and long-term behavior. A review and discussion of these factors will serve as an

introduction to the capping process.

Cap placement. A source of uncontaminated material must be available. Nearby, deeper sediment from the same locale is preferable, however, other sources including upland deposits of sand, silt and clay may be appropriate. In this study it will be assumed that such sources are available and can be placed onto the contaminated sediment to the desired thickness. The development here is concerned with the physicochemical processes of the cap and underlying sediment and not with the procedures or mechanics of creating the cap. For example, it may be necessary to amend the sediment with natural organic matter prior to placement.

Consolidation of sediment. Post capping consolidation of sediment will displace porewater (Sarapas, 1989). This evaluation is based on the assumption that the majority of the upper estuary is underlain by moderately thick (eight or more feet) of soft organic silts (Woodward and Clyde, 1987). It is estimated that an average primary consolidation resulting in 7 to 13 inches downward displacement of the sediment water interface will occur, depending on the thickness of the underlying silt layer. Secondary consolidation, that which occurs over a much longer time period at a much lower rate, will not be addressed. Eleven inches primary consolidation will be assumed in the theoretical study. Based on past sampling (Woodward and Clyde, 1987), Sarapas estimates that, on average, a 10-foot-thick layer is present under the cap and primary consolidation will occur within a period of four months. Based on porosity data, it is expected that porewater from the uppermost sediments will be released most rapidly during consolidation. This displaced water will replace the initial porewater contained within the cap. Sarapas estimates that 6.7 gallons of water per square foot of area is produced upward during primary consolidation and that a 45 cm. cap (25% porosity) contains 2.8 gallons per square foot. He further notes that the displaced porewater is expected to present an ongoing PCB release to the overlying cap in the short-term. Model predictions on this mode of chemical transport to and through the cap will be considered in the next section.

Bed accretion. Some degree of bed accretion will occur after capping. Figure 15 illustrates the bed consolidation process. Relatively clean silts and clays will continue to be deposited and will accumulate on the surface of the cap. These post

capping deposits will contain natural organic matter which will stimulate organism growth and provide sites for absorbing PCBs moving into the capped zone.

Organism recolonization. The zone inhabited by aerobic microorganisms and macrofauna will be translocated upward due to the presence of the cap. Anaerobic organisms may continue to inhabit the original sediment. The net result will likely be a recolonization of surface sediment by organisms. The zone of bioturbation is now within the cap and well away from the PCB contaminated layers. The elimination of organisms in the upper layers of contaminated sediment extinquishes PCB transport by particle movement in this zone and molecular processes prevail.

Long-term behavior. The occurrence of the four events described above has dramatic consequences for PCB transport to the water column. The least of these is the increased chemical diffusive path length provided by the presence of the cap. This path length continues to increase, however, there are practical limits to this. For example, with an initial water depth of one meter, over three thousand years are required to "silt in" the aquatic environment at a constant 3 mm/y bed accretion rate over the period. As will be demonstrated later this time period may be of the order-of-magnitude of the chemical breakthrough time for the original cap depth.

PCB BEHAVIOR DURING PRIMARY CAP CONSOLIDATION

The process of sediment consolidation causes water along the entire length of the column to be squeezed upward. This creates an upward velocity in the sediment and a convective transport of soluble fractions of PCBs in the same direction. For uniform consolidation throughout the sediment column the water velocity is zero at the bottom and a maximum at the top. In the following mathematical analysis it will be assumed that eleven inches of water (~28 cm.) is displaced in the primary consolidation period and that this occurs in a one month period immediately after capping. It will also be assumed that this quantity of water moves through the cap. This time period is a very conservative estimate, choosen to maximize the estimated water flow rate through the cap. (See Figure 15)

Water moving upward percolates through the 30 cm. of contaminated sediment. Here it can pick up quantities of PCBs to the solubility limit. As it emerges from the contaminated

sediment into the cap material fresh sorption sites are available to the leachate. The sites accomodate the PCB molecules and they are removed from solution. It is assumed that the time scale for absorption processes is small compared to the advection time scale. A simple mass balance equates the maximum PCB mass leached to the mass of cap material required to immobilize it. This mass balance yields the minimum chemical penetration depth into the fresh cap material, y_c(cm). The depth relationship is

$$y_c = \Delta v/(1+\rho_B K^*_{A32}) \qquad (20)$$

where Δv is the volume of water displaced (cm^3/cm^2 area) and K^*_{A32} is the PCB partition coefficient for the cap material in L/kg. Table 12 contains the partition coefficients for A-1242 and A-1254 for cap material with 1.0% and 0.2% organic matter.

Calculations were performed with Eq. 20 for Δv=27.94 cm^3/cm^2 (equivalent to 6.7 gallons/ft^2.). For A-1242 y_c=0.071 mm with K^*_{A32}=1980L/kg and 0.35 mm with K^*_{A32}=396 L/kg. For A-1254 y_c=0.026 mm with K^*_{A32}=5390 and 0.13 mm with K^*_{A32}=1078. These calculated results indicate that a cap material containing 0.2 to 1.0% organic matter with ρ_B=2kg/L one millimeter in thickness has the capacity to immobilize all the PCBs flushed from the contaminated sediment during primary consolidation. In the extremely conservative case of K^*_{A32}=1 y_c=9.3 cm. This case is one where the sorptive capacity of the cap material shows no preference for the PCB molecules.

Although the cap material has the capacity to immobilize the PCBs questions concerning the rate of adsorption need to be addressed. Specifically, is the porewater velocity sufficiently slow to allow the molecules time to move from the fluid filled pore channels to solid surfaces where adsorption occurs? Assuming advection is the dominant transport mechanism a PCB differential mass balance in the porespaces yields.

$$\varepsilon\frac{\partial \rho_{A2}}{\partial t} = -\bar{v}\frac{\partial \rho_{A2}}{\partial X} - ka_v(\rho_{A2}-\rho^*_{A2}) \qquad (21)$$

where $\bar{v}$ is the apparent fluid velocity (i.e. 27.94cm/30d) of 0.93cm/d, k is the transport coefficient within the porous bed, cm/d, and a_v is the external surface area [$a_v=6(1-\varepsilon)/d$, where d is particle diameter], cm^2/cm^3. The three terms in Eq. 21 are: accumulation in the pore spaces, advection and transport to the sorptive walls of the porous media. Non-dimensionalizing Eq. 21 yields

$$\frac{\partial \rho}{\partial T} = - \frac{\partial \rho}{\partial X} - \left[\frac{rka_v}{\bar{v}}\right] (\rho-\rho^*) \qquad (22)$$

where ρ, T and X are dimensionless concentration, time and distance. The terms in the bracket are the scaling ratio

$$R \equiv rka_v/\bar{v} \qquad (23)$$

which is the ratio of the chemical transport toward the solid surfaces to the rate of chemical advection. Large values of R suggest that the PCBs are retained in the bed and not swept through and out by the percolating water.

Calculations were based on an apparent fluid velocity of 0.93cm/d. This value is likely an upper bound velocity which exaggerates the advective process. Sarapas (1989) suggests four months (120d) rather than one for primary consolidation. A correlation for packed beds from Treybal (1980) was used to estimate k. Calculations for particle diameters of 1.0mm and 0.1mm yielded R values of 20 and 93 respectively. So it appears that the rate of PCB movement to the sediment surface is much more rapid than down the pore channels. The Reynold numbers Re, for the particles are 4.3E-4 and 4.3E-5 respectively indicating laminar flow.

Dispersion in the axial direction should be addressed. This transport mechanism is common in porous media and is the result of different porewater velocities in the network of pore channels. It is generated by the advection process. Perry and Chilton (1973) report that the axial dispersion Peclet Number, Pe, for liquids in packed beds under laminar flow (Re<20) is 0.5. Since $Pe=r\bar{v}/2D_{A3y}$ this indicates that dispersive transport dominates advective transport only by a factor of 2. Even with

this enhancement of transport in the porewater flow direction since R values are so large chemical movement to the walls is highly favored.

In summary, the analyses performed in this section suggest that the PCBs which emerge from the contaminated sediment are immobilized onto solid surfaces after moving only a very short distance into the cap material. Accounting for advection and dispersion and due to the sorptive capacity of the cap material the distance of penetration is expected to be of the order of one centimeter or less. A comprehensive mathematical model of the consolidation process is needed to verify the results of the above analysis which is based entirely on vignette models.

PCB BREAKTHROUGH TIMES FOR THE CHEMICAL BARRIER

The 45 cm. cap illustrated in Figure 15 contains two layers. The upper layer, shown as 10 cm., is to mitigate the effects of bioturbation and to confine these to a region well away from the contaminated sediment. An assumed 20 cm. layer for the benthic community is even more conservative. The remaining depth of sediment is to serve as the chemical barrier. This thickness will likely be 25 to 35 cm. In order to appreciate the effectiveness of this layer breakthrough times for 10 cm. to 35 cm. will be considered in the following analysis.

The theoretical model for PCB transport in the chemical barrier without advection are contained in Equations 4 and 5 on page 6. The model is based on transient molecular diffusion through a sorptive porous medium. The semi-infinite slab boundary conditions provides a realistic solution to Equation 4. The solution is (Formica, et.al., 1988):

$$t_b = \left[y \ \mathrm{erf}^{-1}\{(\rho^*_{A2} - \rho_{A2i})/\rho^*_{A2}\} \right]^2 / 4D_{eff} \qquad (23)$$

where t_b is chemical breakthrough time, seconds, y is the chemical barrier thickness, cm., erf^{-1} is the inverse error function, ρ^*_{A2} is the chemical concentration in the contaminated sediment pore water, g/cm^3 and ρ_{A2i} is the chemical concentration at the boundary between the chemical barrier and

the bioturbation layer.

It will be assumed that the contaminated sediment zone below the cap contains a sufficient quantity of PCBs such that the concentration at the bottom surface of the cap (i.e., ρ^*_{A2}) is always constant and at the solubility limit. This is the source concentration. Breakthrough is assumed to occur at the upper surface of the chemical barrier when the concentration within the porewater is at a value equal to the current EPA chronic criteria for aquatic life, 30 ng/L (EPA, 1986). Based on the solubility values in Table 5 the erf^{-1} values are 2.5 and 2.2 for A-1242 and A-1254 respectively.

The use of the above two assumptions on in-bed concentration tends to maximize the actual chemical gradient through the upper estuary. Since only a fraction of the sediment is contaminated to the extent that the solubility condition is achieved, ρ^*_{A2} is maximum. PCB breakthrough is assumed to have occured when a concentration of 30 ng/L is achieved within the bed at a depth of 10 cm. Actual PCB breakthrough, that emerges in the water column, occurs at a later time. So this approach tends to underestimate the actual breakthrough time.

It was demonstrated in the previous section that the consolidation process moves some fraction of the PCBs into the cap very quickly. This advective transport process reduces the effective chemical barrier thickness, y, in Equation 23. To account for this effect Equation 20 is combined with 23 to yield

$$t_b = \left[\{ y - \Delta v / (1 + \rho_B K^*_{A32}) \} / 2.5 \right]^2 / 4 D_{eff} \qquad (24)$$

for A-1242. D_{eff} values are from Table 12. Calculated breakthrough times for off-site sand cap material based on Equation 24 are displayed graphically as a function of chemical barrier depth in Figure 17. Table 18 summarizes these times. A-1242 breaks through first and the 0.2% organic matter cap matterial is less effective than the 1.0% organic matter. For a 35 cm. chemical barrier depth approximately 900 years lapse before A-1242 breaks through. A time period in excess of 15,000 years is required for A-1254 with a 1% organic matter and 35 cm. barrier.

The above breakthrough time results are for a proposed off-site sand as the cap material. Another choice for this cap material may be the silty sediment from the New Bedford Harbor. This material as it exists in the estuary is very porous, ε=0.67, with bulk (dry) density of 0.75 g/cm^3. Based on the analysis of the "diffusion tails" on p. 10 direct evidence exists on the effective diffusivities, D_{eff}, for both aroclors in the silty estuary sediment (see Table 7). Breakthrough times based on average D_{eff}=6.2E-9cm/s for A-1242 and 4.6E-9cm^2/s for A-1254 also appear in Figure No. 17. The calculated times for the silty estuary sediment are less than that for the off-site sand at equal barrier depths. The reason for this is likely the porous nature of the silt. According to Equation 5 $D_{eff} \sim \varepsilon^{4/3}/\rho_B$. If the silt could be compacted to the same degree as the sand to yield ε=.25 and ρ_B=2.0 g/cm^3, D_{eff} would be reduced by a factor of 1/10 based on Equation 5. The breakthrough times shown for the silty estuary sediment in Figure 17 would correspondingly increase by a factor of ten. The net result being a cap made of compacted silty estuary sediment would have similar breakthrough time characteristics as the proposed cap made of off-site sand.

Also shown in Figure 17 are the computed breakthrough times for a non-adsorptive sediment. For K^*_{A32}=1 breakthrough occurs in a few days. In the calculations the bed porosity was 25% and bulk density 2.kg/L.

In summary, the analysis performed in this section suggest that a 25 to 35 cm. chemical barrier containing 0.2 to 1.0% organic matter is very effective in isolating the PCB from the water column. The key assumption that makes isolation possible is that the transport process is by molecular diffusion. There is some evidence that this is presently the case in sediments of the upper estuary at the 15 cm. depth and deeper. (see p. 10 on analysis of the "diffusion tails")

CALCULATED PCB RELEASE RATES FROM A CAPPED SEDIMENT BED

Based in part on the laboratory testing results reported above by Brannon et al. (1985) and Sturgis and Gunnison (1988) a base capping scenario was chosen. The proposed cap for the base

case consists of a 45 cm. thick layer of which 35 cm. is to serve as a chemical barrier and 10 cm. above this to mitigate the effects of bioturbation. The relative positions of the three layers that include the original contaminated sediment is illustrated in Figure 14b. Other cases, such as a 25 cm. chemical barrier and 20 cm. bioturbed layer, will also be considered.

The type of material to be used to construct the cap will consist of a poorly graded, medium-grained sand and some fine-grained sand and silt. It is expected that the cap material will possess an organic content of less than 1% although greater than 0.2%. As noted above, due to the nature of the cap material proposed, rapid consolidation of the cap is expected and the resultant effective pore space will be in the range of 20 to 30%.

Equations 11 and 12 apply to the steady-state flux condition. The steady-state flux is effective after breakthrough occurs. At steady-state the chemical flux rate through the cap is at its maximum value. The PCB molecules must move through the 35 cm. chemical barrier by molecular transport processes, move by bioturbated sediment processes through the next 10 cm. and finally move through the benthic boundary layer on the water side. Equation 12 accounts for these three resistances in series. Calculations indicate that the molecular process accounts for $\geq$99.5% of the resistance to transport through the cap. This resistance term is the last one on the rhs of Equation 12 and constitutes the "chemical barrier" property of the cap.

The concentration range of total PCBs on the original bed sediment is considerable: ω_A=10 to 25,000 ppm. Due to the solubility limit concept, the concentration range in solution adjacent to the particles is much less. At the 45 cm depth level the maximum concentration of A-1242 is 0.088 mg/L and that for A-1254 is 0.012 mg/L. Since molecular diffusion is the transport process at this level and up to the 10 cm. level, ρ^*_{A2} values can go no higher than the above values. This thermodynamic restriction effectively lowers the flux rate through the chemical barrier because it places a limit on the concentration "driving force" (i.e., $\rho^*_{A2}-\rho_{A2}$) in Equation 11. The consequence of placing the contaminated sediment deep enough so as to be beyond the reaches of the particle transport process

of organisms is to dramatically lower the release rate. Table 12 contains various parameters used in the steady-state flux calculation. The molecular diffusivities, $\mathcal{D}_{A2}$, are from Thibodeaux (1989). Equation 5 was used for computing the effective diffusivity, D_{eff}, values.

From a detailed analysis on the rate of dissipation of the Aroclors from the contaminated zone it was found that only 4 to 14% would be lost over 10,000 years (see Appendix B). This suggests that ρ^*_{A2} will remain virtually constant in the original contaminated zone after capping and the steady-state flux will therefore be the maximum rate. Steady-state emission rates after capping were computed with the equation:

$$W_A = {}^2K'_{A3} f_A A (\rho^*_{A2} - \rho_{A2}) \qquad (25)$$

with ρ_{A2}, the PCB concentration in the water column, assumed to be 0.0 ppm. The isopleth concentrations and fractional areas used in Part II are also used in this computation.

The computed emission rate values for the base case capping scenario appear in Table 13. Also in the table are the ρ^*_{A2} values. Note that these values are constant above ω_A=300 ppm for A-1242 and above ω_A=75 ppm for A-1254. For convenienve Aroclor-1248 was assumed to have the A-1254 porewater concentration values however, the actual f_A values from Table 3 were used. The total PCB emission rate after capping is to be the sum of the three primary Aroclors. This is 196 g/y. Based on the sediment-side flux values, this steady-state value is 0.012% of the present W_A (min) and 0.0023% of the present W_A (ave) emission rates. Interpreted in terms of reducing the present release rates, the cap has an efficiency in the range of 99.988% to 99.998%.

Emission rates for alternative capping scenarios can be determined from the inverse ratio of the chemical barrier depths. For example, the total PCB flux rate for a 25 cm. chemical barrier depth is (35/25) X 196=274g/y. From above the base case flux is 196g/y for 35 cm. The reason this simple inverse depth ratio conversion applies is that greater than 99% of the chemical transport resistence resides in the chemical

barrier where the integrated form of Fick's first law (Equation 3) applies. Based on the present sediment-side flux, $\sigma_A(min)$ = 1674 kg/y the 25 cm. chemical barrier is also effective in reducing the total PCB flux by greater than 99.9%.

Using the steady-state flux it is possible to estimate sediment and pore water concentrations in the bioturbated zone. The relationship for computing the porewater concentration at depth y(cm.) is:

$$\rho_{A2}(y) = n_A/(1/^3k'_{A2}+y/\rho_B\Sigma_{A3}^{(t)}K^*_{A32}) \qquad (26)$$

This calculation was performed for the base case at the y=2 cm. and y=10 cm. plane depth in the cap and the results appear in Table 14. The first two columns are for the 2 cm. depth and the other two columns are for the 10 cm. depth below the sediment/water interface. These Aroclor concentrations on the sediment are low. For A-1242 this is approximately 2/10ths of a ppm. and for A-1254 this is approximately 3/100ths of a ppm. These concentrations are uniform throughout the 2 cm. depth plane of the Upper Estuary because of the solubility limit and therefore represent maximum values.

PART IV
CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations are divided into two parts. The first part is concerned with the present situation in the Upper Estuary with respect to the PCB contaminated bed-sediment. The second is concerned with the proposition of capping the contaminated sediment with clean sediment. The presentation format is a listing of items; conclusions are listed first followed by recommendation.

THE PRESENT SITUATION

- ⊗ The dominant PCB transport mechanism from sediment to water is via bioturbation processes which primarily occur in approximately the top 3 to 10 cm.
- ⊗ Based on the results of three chemodynamic models, the annual total PCB quantity leaving the bottom sediment is likely in the range of 500 to 6000 kg.

- At lease forty percent of the PCB entering the water column from the bed sediment evaporates to the air and the remainder leaves via the water route under the Coggeshall Street Bridge.
- Sediment contaminated at and above 5000 ppm. involves 9 acres in area but constitutes 30% of the PCB source. That contaminated at and above 100 ppm. involves 110 acres and constitutes 97% of the source.
- Analysis of in situ bioturbation processes and additional thin layer sediment samples will allow a more precise estimate of the current release rate.
- In-situ measurements using the so called flux chamber should be performed as an independent check of the release rate.
- Future modeling efforts should concentrate on details of the evaporation process.

THE CAPPING PROPOSAL

- Theoretically, capping with clean sediment to a depth of 45 cm. is effective and greater than 99.9% reduction in the present PCB release rate is possible.
- PCB breakthrough will require the order of 4,500 years for a cap consisting of 1% organic matter and 900 years for 0.2% organic matter.
- The steady state flux rate through this cap would be 200 to 270 g/y.
- At breakthrough, and/or the steady-state flux condition, the PCB on sediment concentration in the top two centimeters will be 200 ppb for A-1242 and 28 ppb for A-1254 with the base case.
- The efficacy of capping in controlling the PCB release rate needs to be verified in the laboratory. The following hypotheses concerning PCB transport in capped scenarios need to be tested:
  a. At steady-state, transport in the molecular diffusion zone is solution driven and the flux rate is constant for sediment contamination levels above the solubility limit.

  b. The steady-state flux rate is independent of the organic matter or clay content of the material.

c. The times necessary for breakthrough are long and dependent on the organic matter or clay content of the cap material.

d. Rapid sediment consolidation does not release significant quantities to the water column.

TABLE 1
NEW BEDFORD HARBOR
THIN LAYER SEDIMENT SAMPLING PROGRAM
PCB ANALYSES

SAMPLE DESIGNATION	SAMPLE DEPTH(cm)	AROCLORS 1242/1016(ppm)	AROCLOR1254(ppm)
FX - 1	0 - 1	1,300	300
FX - 2	1 - 2	1,100	230
FX - 3	2 - 3	1,800	350
FX - 4	3 - 4	2,900	390
FX - 6	4 - 6	3,300	480
FX - 8	6 - 8	5,600	740
FX - 10	8 - 10	6,300	900
FX - 12	10 - 12	5,700	870
FX - 14	12 - 14	2,600	1,400
FX - 16	14 - 16	3,700	1,400
FX - 20	16 - 20	1,300	1,200
FX - 24	20 - 24	480	1,000
FX - 28	24 - 28	28	260
FX - 32	28 - 32	3.8	27
FX - 36	32 - 36	0.1	0.09
FX - 40	36 - 40	0.08	0.02
FX - 44	40 - 44	0.12	0.02
FX - 48	44 - 48	0.22	0.04
FX - 52	48 - 52	0.32	0.04
FX - 56	52 - 56	0.45	0.08
FX - 60	56 - 60	ND(0.01)	ND(0.01)
FX - 64	60 - 64	ND(0.1)	ND(0.1)

Notes: 1) All concentrations are in milligrams per kilogram (ppm) dry weight basis.

2) ND (-) means not detected (at instrument detection limit).

TABLE 1 (CONTINUED)

SAMPLE DESIGNATION	SAMPLE DEPTH(cm)	AROCLORS 1242/1016(ppm)	AROCLOR 1254(ppm)
DR - 1	0 - 1	160	61
DR - 2	1 - 2	210	80
DR - 3	2 - 3	160	59
DR - 4	3 - 4	130	50
DR - 6	4 - 6	140	64
DR - 8	6 - 8	210	95
DR - 10	8 - 10	170	87
DR - 12	10 - 12	140	58
DR - 14	12 - 14	110	49
DR - 16	14 - 16	90	54
DR - 18	16 - 18	49	34
DR - 20	18 - 20	23	12
DR - 22	20 - 22	6.8	2.5
DR - 24	22 - 24	4.1	0.92
DR - 26	24 - 26	0.4	0.14
DR - 28	26 - 28	1.2	ND(0.1)
DR - 30	28 - 30	ND(NR)	ND(NR)
DR - 32	30 - 32	ND(0.05)	ND(0.05)
DR - 36	32 - 36	ND(0.05)	ND(0.05)
DR - 40	36 - 40	ND(0.05)	ND(0.05)
DR - 44	40 - 44	ND(0.05)	ND(0.05)
DR - 48	44 - 48	ND(0.05)	ND(0.05)

Notes: 1) All concentrations are in milligrams per kilogram (ppm) dry weight basis.

2) ND (-) means not detected (at instrument detection limit).

3) NR means detection limit not reported.

Table 2 Site FX Data vs the Box Model

Parameter	Aroclor 1242	Aroclor 1254
slope, 1/cm	.175	.118
$^{3}k'_{A2}/K^{*}_{A32}\rho_B$	3.10	1.14
h(Δ=1cm/y)	23.4	18.1
h(Δ=.33 cm/y)	59.4	37.8
h($^{3}k'_{A2}$=0)	5.71	8.74

Table 3. Sediment Area vs PCB Concentration

Concentration Range ω_A (ppm)	Fractional Surface Areas			
	Aroclor 1016/1242	Aroclor 1248	Aroclor 1254	Total PCBs
0-10	.1885	.5014	.2551	.1502
10-50	.1655	.2140	.2463	.1500
50-100	.1186	.1116	.1349	.1171
100-500	.3386	.1500	.2396	.2831
500-1000	.0635	.0186	.0442	.1429
1000-2000	.0382	.00	.0459	.0484
2000-5000	.0609	.0044	.0283	.0617
5000-10,000	.0179	.00	.0057	.0313
10,000-15,000	.0050	.00	.00	.0081
15,000-25,000	.0027	.00	.00	.0068
>25,000	.00	.00	.00	.0005
	1.0000	1.0000	1.0000	1.0000

Table 4. PCBs - Key Chemical Properties

Aroclor	K_{OC} L/kg	Solubility mg/L	Average mol.wt.
1242	180,000	0.24	266.5
1248	580,000	0.054	299.5
1254	490,000	0.030	238.5

K_{OC} - soil ads, constant ref. to organic matter

Table 5 Chemical Properties in Sea Water

Aroclor	K^*_{A32} (L/kg)	Solubility (mg/L)
1242	7920	.088
1248	25,520	--
1254	21,560	.012

$K^*_{A32} = K_d$ in common nomenclature.

Table 6 Biodiffusion Coefficients

Source	Site	Depth of Bioturbated Layer(cm)	$\mathfrak{D}^{(t)}_{A3}$ (cm^2/y)
Appendix A	Upper Estuary	10-13*	3.36 to 7.1
Aller (1982)	Narragansett Bay	0-9	5 to 32
Brownawell (1986)	Buzzards Bay	10	9.4
Thibodeaux+	Upper Estuary	8	9 - 13

+Based on Spaulding's (1987;p.72) tabulate average A-1254 concentrations; 511 μg/g at 2 cm., 2681 at 4 cm., an assumed 10,000 μg/g at 8 cm., t=1982-1977=5y and Crank's (1975) model for diffusion from a plane sheet (Figure 4.1, p. 50) without bed accretion.

*Figure 1 in Appendix A.

Table 7 Analysis of Downward Diffusion Tails

Sample Site FX				Sample Site DR			
Depth, y (cm)	$1-\omega_A/\omega_A^o$	$y/\sqrt{4\mathcal{D}_{A3}t}$	$\mathcal{D}_{A3}$XE9 (cm^2/s)	Depth (cm)	$1-\omega_A/\omega_A^o$	$y/\sqrt{4\mathcal{D}_{A3}t}$	$\mathcal{D}_{A3}$XE9 (cm^2/s)
0+	.00*	.00	--	0+	0*	0	--
3	.65	.66	3.90	2	.46	.44	3.9
7	.87	1.07	8.08	4	.74	.80	4.7
11	.992	1.88	6.46	6	.92	1.24	4.4
15	.999	2.35	7.69	8	.95	1.39	6.2
19	.99997	2.95	7.83	10	.9956	1.99	4.7
				12	.987	1.76	8.6
	Aroclor 1242 ave=6.8 σ=1.7				Aroclor 1242 ave=5.4 σ=1.7		
0+	.00*	.0	--	0+	0*	0	--
3	.60	.595	6.36	2	.37	.34	6.5
7	.67	.69	25.7	4	.78	.87	4.0
11	.91	1.2	21.0	6	.95	1.38	3.2
15	.991	1.84	16.1	8	.98	1.64	4.5
19	.99999	3.1	9.39	10	.997	2.0	4.7
	Aroclor 1254 ave=15.8 σ= 8.0				Aroclor 1254 ave=4.6 σ=1.2		

+Zero represents 15 cm. depth in Table 1. *ω_A^o values at 15 cm. depth in Table 1 except A-1254 at FX; ω_A^o=3000 μg/g. (assumed).

Table 8 PCB FLUX RATE PREDICTIONS AT SITES FX AND DR

Model Type	Site	Flux ($mg/cm^2 \cdot y$) A-1242/1016	A-1254
transient; Eq. 9 App. B.	FX	2.89	0.76
steady-state; Eq. 15	FX	2.59	.602
steady-state; Eq. 14	FX	3.00	.353
steady-state; Eq. 15	DR	.0919	.0268
steady-state; Eq. 14	DR	.353	.0429

Table 9 Aroclor Emission Rates for 1985-86

$\bar{\omega}_A$ (ppm)	Rates from sediment to water in kg/y Aroclor 1242	Aroclor 1248	Aroclor 1254
5	-1.7	-1.1	-0.6
30	38	30	37
75	73	44	58
300	874	250	433
750	413	7.3	202
1,500	498	0	412
3,500	1856	87	607
7,500	1170	0	262
12,500	610	0	0
17,500	412	0	0
25,000	0	0	0
	5942	417	2010

Table 10 Total PCB Emission Rate, New Bedford Harbor Upper Estuary 1985 - 1986

Concentration range (ppm)	Sediment Area f* %	Σf %	Rate Kg/y	Rate ÷ Total %	Σ Rate ÷ Total %
0-10	15.02	100.01	-3	-.00	99.99
10-50	15.00	84.99	105	1.25	100.
50-100	11.71	69.99	175	2.09	98.8
100-500	28.31	58.28	1557	18.60	96.7
500-1000	14.29	29.97	622	7.43	78.1
1000-2000	4.84	15.68	910	10.87	70.6
2000-5000	6.17	10.84	2548	30.45	59.8
5000-10,000	3.13	4.67	1432	17.11	29.3
10,000-15,000	0.81	1.54	610	7.29	12.2
15,000-20,000	0.68	0.73	412	4.92	4.92
>25,000	0.05	0.05	**	**	**
	100.01		8369	100.01	

**Rate is sum of individual Aroclors of concentrations on Figures 1, 2 and 3. Concentration values do not exceed 15,000.

*Fractional areas based on Figure 4 and concentration values ranged to 25,000. So this is why the >25,000 line has area but no rate.

Table 11 Uncertainty Intervals for Selected Data and Calculated Results

Input data: Variable	$\mathfrak{D}_{A3}^{(t)}$ (cm^2/y)	y_b (cm)	$\rho_B f_A A2 \bar{\omega}_A$ ($\mu g/cm$)
average value	10	10	1
uncertainty interval	3 to 15	5 to 15	1 ± 0.05
relative error	±6/10	±5/10	±1/20

Output data: emission rate	W_A(min)	W_A(ave)	W_A(max)
Kg/y	1674	8369	15,550

Table 12 Transport Parameter for the Cap Material Calculations

Aroclor	K^{*}_{A32} (L/kg) 1.0%	K^{*}_{A32} (L/kg) 0.2%	$\mathcal{D}_{A2}$ (cm^2/s)	D_{eff} (cm^2/s) 1.0%	D_{eff} (cm^2/s) 0.2%	$^{3}K'_{A2}$ (cm/y) 1.0%	$^{3}K'_{A2}$ (cm/y) 0.2%
1242	1980	396	.45E-5	3.41E-10	17.0E-10	.64	.64
1254	5390	1078	.48E-5	1.31E-10	6.68E-10	.68	.68

Table 13 Aroclor Emissions after Capping*

$\bar{\omega}_A$ (ppm)	ρ^{*}_{A2} A-1242 (ppm)	W_A A-1242 (g/y)	ρ^{*}_{A2} A-1254 (ppm)	W_A A-1254 (g/y)	W_A A-1248 (g/y)
5	.00063	.58	.00022	.29	.58
30	.0038	3.1	.0014	1.80	1.57
75	.0095	5.55	.0035	2.47	2.04
300	.038	63.3	.012	15.0	9.41
750	.088	27.5	.012	2.77	1.17
1500	.088	16.5	.012	2.88	.0
3500	.088	26.4	.012	1.78	.27
7500	.088	7.75	.012	.36	.0
12,500	.088	2.17	.012	.0	.0
17,500	.088	1.17	.012	.0	.0
25,000	.088	.0	.012	.0	.0
		154.		27.4	15.0

*35 cm. chemical barrier depth.

Table 14 PCB Concentrations at the 2 cm. and 10 cm. Depth vs % Organic Matter in Sediment Cap.

Aroclor	c^*_{A2}(mg/L)		c^*_A(mg/L)	
	at 2 cm. for		at 10 cm. for	
	1.0%	0.2% O.M.	1.0%	0.2% O.M.
1242	.042	.037	.18	.18
1254	.0076	.0057	.028	.026

TABLE 15 Water Flow-by-Concentration Model
Coggeshall Street Bridge Transect (ASA-1989)

Study	Date	Net Seaward PCB Rate (kg/y)	Estimated Release from Bed Sediment (kg/y)*	(kg/y)**
WES	6-3-86	49.3	99	237
	24-4-86	1663.8	3330	7990
	5-6-86	1561.1	3120	7490
EPA	10-1-83	578.1	1160	2770
	11-1-83	698.1	1400	3350
	11-1-83	641.1	1280	3080
ASA	16-11-88	106.5	213	511
	22-11-88	1290.1	2580	6190
	2-12-88	67.7	135	325
	9-12-89	82.5	165	396
	10- 1-89	248.8	498	1190
	8- 2-89	107.9	216	518

*Release from bed = 2 X net seaward.

**Release from bed = 4.8 X net seaward

TABLE 16 Evaporation Parameters

Wind (m/s)	K_e	100E (m/d) (%)	$t_{1/2}$ (h)	$1+K_eAQ$
7	1.68	41.2	9.0	1.7
10	2.37	49.8	6.4	1.99
15	6.00	71.5	2.5	3.51
20	9.12	79.2	1.7	4.80

$E \equiv K_e/(K_e + Q_u/A)$, fraction evaporated.

*Coeffs from Figure 4.2-3, page 184, Thibodeaux (1979)

$t_{1/2} = .693\ \text{depth}/K_e$, Equation 4.2-8, page 176, Thibodeaux (1979)

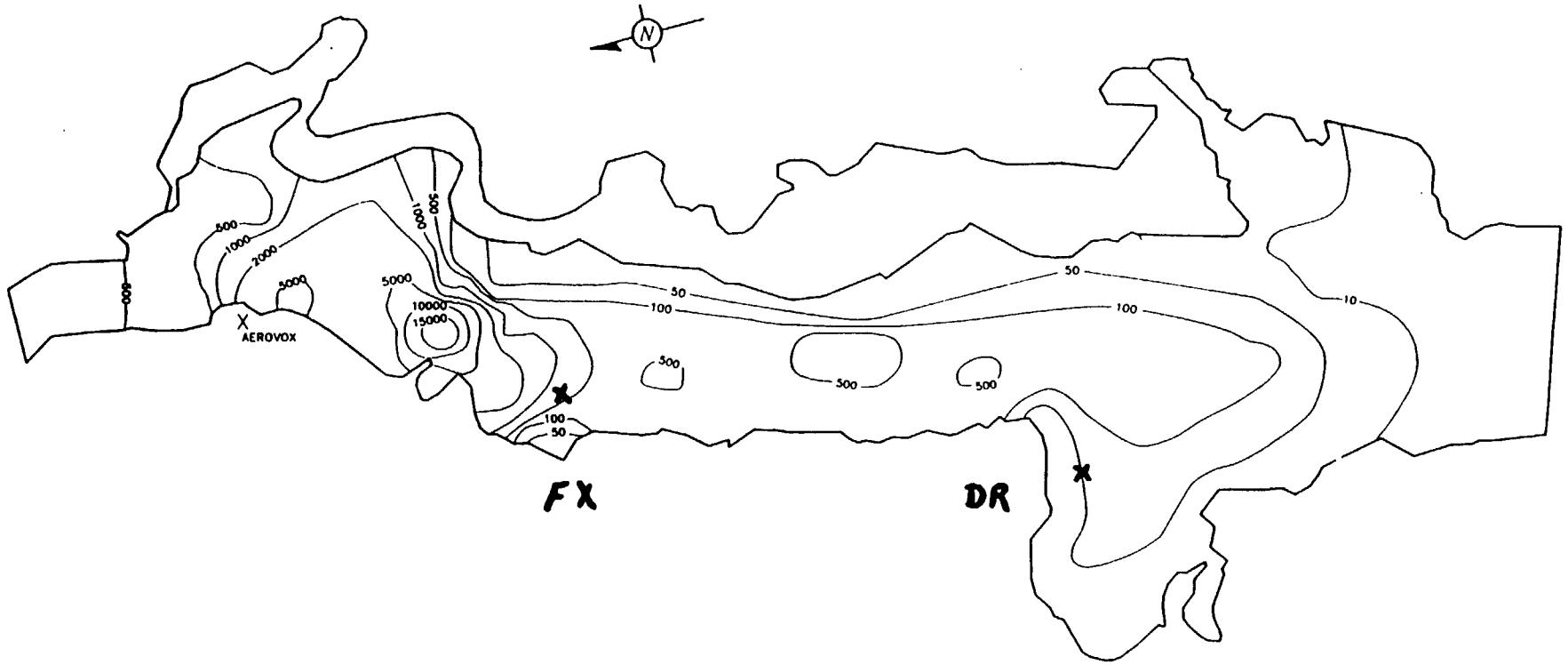
TABLE 17 Model Confidence Analysis

Model and Key Parameters	Parameter Certainty
Bed sediment transport (Eq. 16)	
PCB concentration by area	GOOD
bioturbation depth	POOR
bioturbation coefficient	POOR
Estuary mass balance (Eq. 19)	
annual tidal exchange volume*	GOOD
PCB concentration in water	GOOD
evaporation coefficient	AVERAGE
Water flow-by-concentration (Eq. on P.25)	
PCB concentration in water	GOOD
velocity·concentration·area product	AVERAGE to GOOD
evaporation coefficient	AVERAGE

*This parameter is the basis for defining "good".

TABLE 18 Breakthrough Times for Chemical Barrier

Chemical Barrier Depth, cm	Breakthrough time in years for A-1242 0.2% organic matter	A-1242 1.0% organic matter	A-1254 0.2% organic matter	A-1254 1.0% organic matter
10	74	371	245	1250
20	297	1487	980	5000
30	670	3346	2205	11,251
35	912	4555	3001	15,314



LEGEND:

—500— = A1016/1242 CONCENTRATION ISOPLETH (PPM)

NOTES:

1) ISOPLETHS DEVELOPED USING KRIGING & DATA FROM UNITED STATES ARMY CORPS OF ENGINEERS (AUGUST-OCTOBER, 1985) AND BATTELLE/NUS (JUNE, 1985)

DRAFT

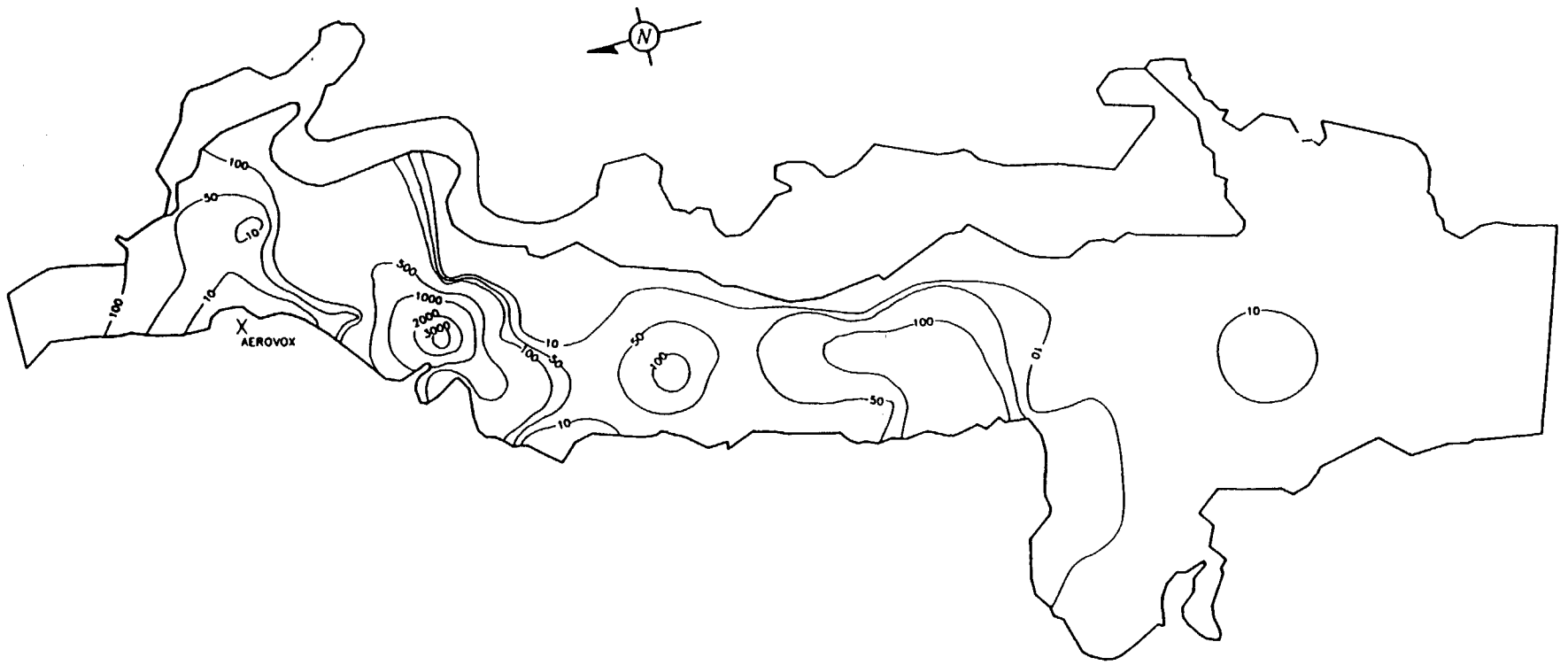
Figure 1

BALSAM
ENVIRONMENTAL CONSULTANTS, INC.
58 STILES RD. SALEM, N.H. 03079

CLIENT: NUTTER, MCLENNEN AND FISH

TITLE: ISOPLETHS FOR A1016/1242 CONCENTRATIONS 0-12' INTERVAL

DATE	DRAWN	DESIGNED	PROJECT
	D.J.P.	E.S.W.	NEW BEDFORD HARBOR
APPROXIMATE SCALE:	F.I.S. NO. 6002ue23	APPROVED L.C.S.	VOLUME NO. / PROJECT NO.



LEGEND:

—100— = A1248 CONCENTRATION ISOPLETH (PPM)

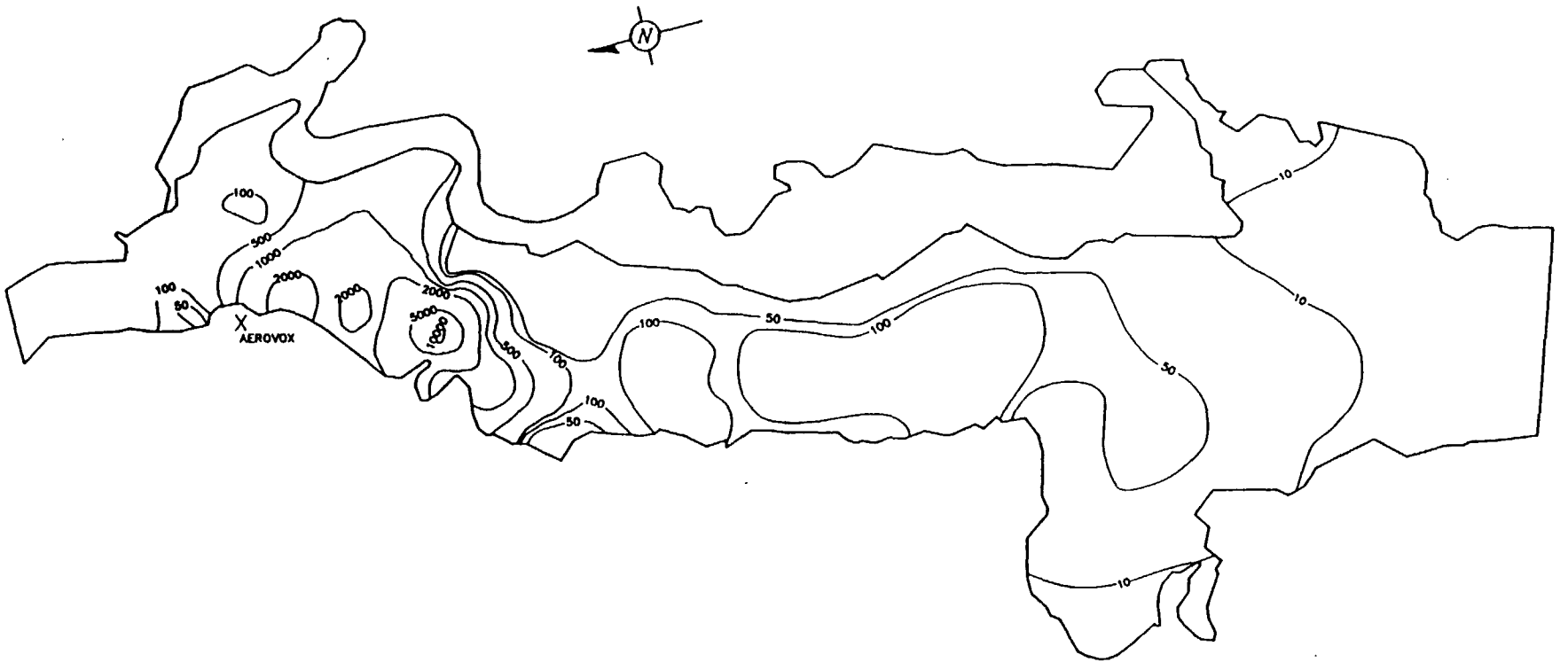
DRAFT

Figure 2

NOTES:

1) ISOPLETHS DEVELOPED USING KRIGING & DATA FROM UNITED STATES ARMY CORPS OF ENGINEERS (AUGUST–OCTOBER, 1985) AND BATTELLE/NUS (JUNE, 1985)

BALSAM ENVIRONMENTAL CONSULTANTS, INC 50 STILES RD. SALEM, N.H. 03079			CLIENT: NUTTER, MCLENNEN AND FISH
			TITLE: ISOPLETHS FOR A1248 CONCENTRATIONS 0–12" INTERVAL
DATE:	DRAWN: D.J.P.	CHECKED: E.S.W.	PROJECT: NEW BEDFORD HARBOR
APPROXIMATE SCALE: [redacted]	FILE NO: 6002ue24	APPROVED: L.C.S.	DRAWING NO. / PROJECT NO.



LEGEND:

100 = A1254 CONCENTRATION ISOPLETH (PPM)

DRAFT

Figure 3

NOTES:

1) ISOPLETHS DEVELOPED USING KRIGING & DATA FROM UNITED STATES ARMY CORPS OF ENGINEERS (AUGUST-OCTOBER, 1988) AND BATTELLE/NUS (JUNE, 1985)

BALSAM ENVIRONMENTAL CONSULTANTS, INC. 98 STILES RD. SALEM, N.H. 03079			CLIENT: NUTTER, MCLENNEN AND FISH
			TITLE: ISOPLETHS FOR A1254 CONCENTRATIONS 0-12" INTERVAL
DATE:	DRAWN: D.J.P.	CHECKED: E.S.W.	PROJECT: NEW BEDFORD HARBOR
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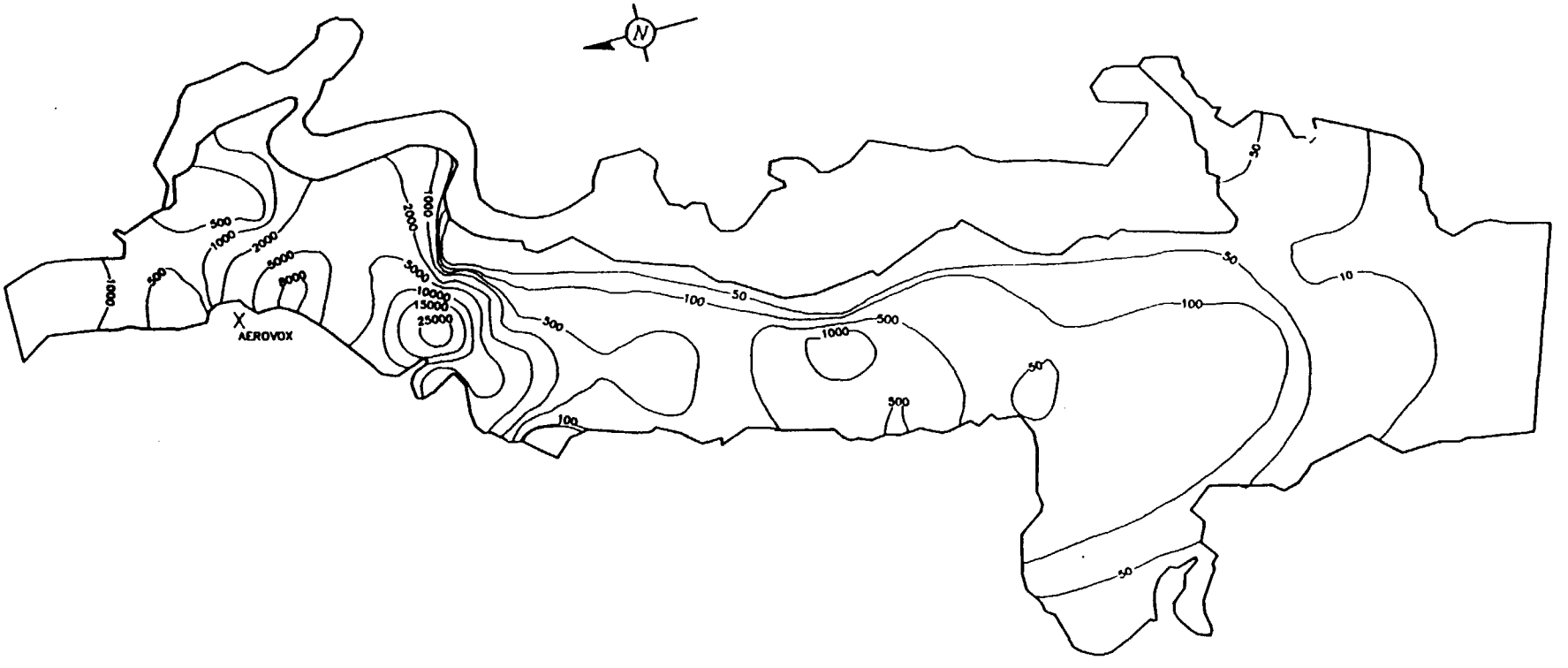
			PROJECT NO:



LEGEND:

—100— = TOTAL PCB CONCENTRATION ISOPLETH (PPM)

DRAFT

Figure 4

NOTES:

1) ISOPLETHS DEVELOPED USING KRIGING & DATA FROM UNITED STATES ARMY CORPS OF ENGINEERS (AUGUST–OCTOBER, 1985) AND BATTELLE/NUS (JUNE, 1985)

BALSAM
ENVIRONMENTAL CONSULTANTS, INC.
30 STILES RD. SALEM, N.H. 03079

CLIENT: NUTTER, MCLENNEN AND FISH

TITLE: ISOPLETHS FOR TOTAL PCB CONCENTRATIONS 0'-12' INTERVAL

DATE:	DRAWN: D.J.P.	REVIEWED: E.S.W.	PROJECT: NEW BEDFORD HARBOR
APPROXIMATE SCALE: -	FILE NO.: 8002ue28	APPROVED: L.C.S.	FIGURE NO.:	PROJECT NO.:

Figure 5 Concentration Profile

Aroclors 1242/1016○; 1254•

New Bedford

Sample Station FX

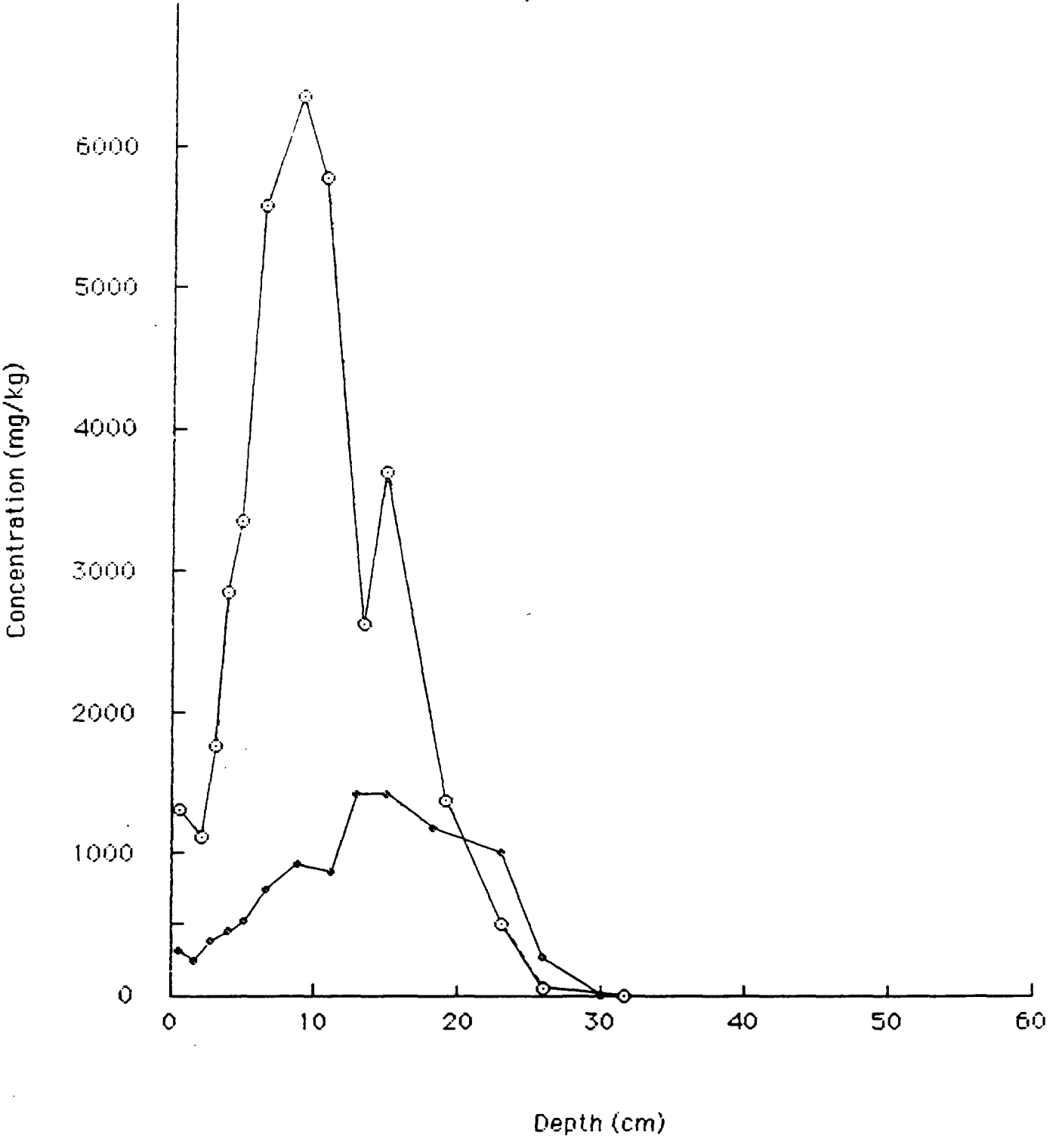


Figure 6 Concentration Profile

Aroclors 1242/1016⊙; 1254•
New Bedford
Sample Station DR

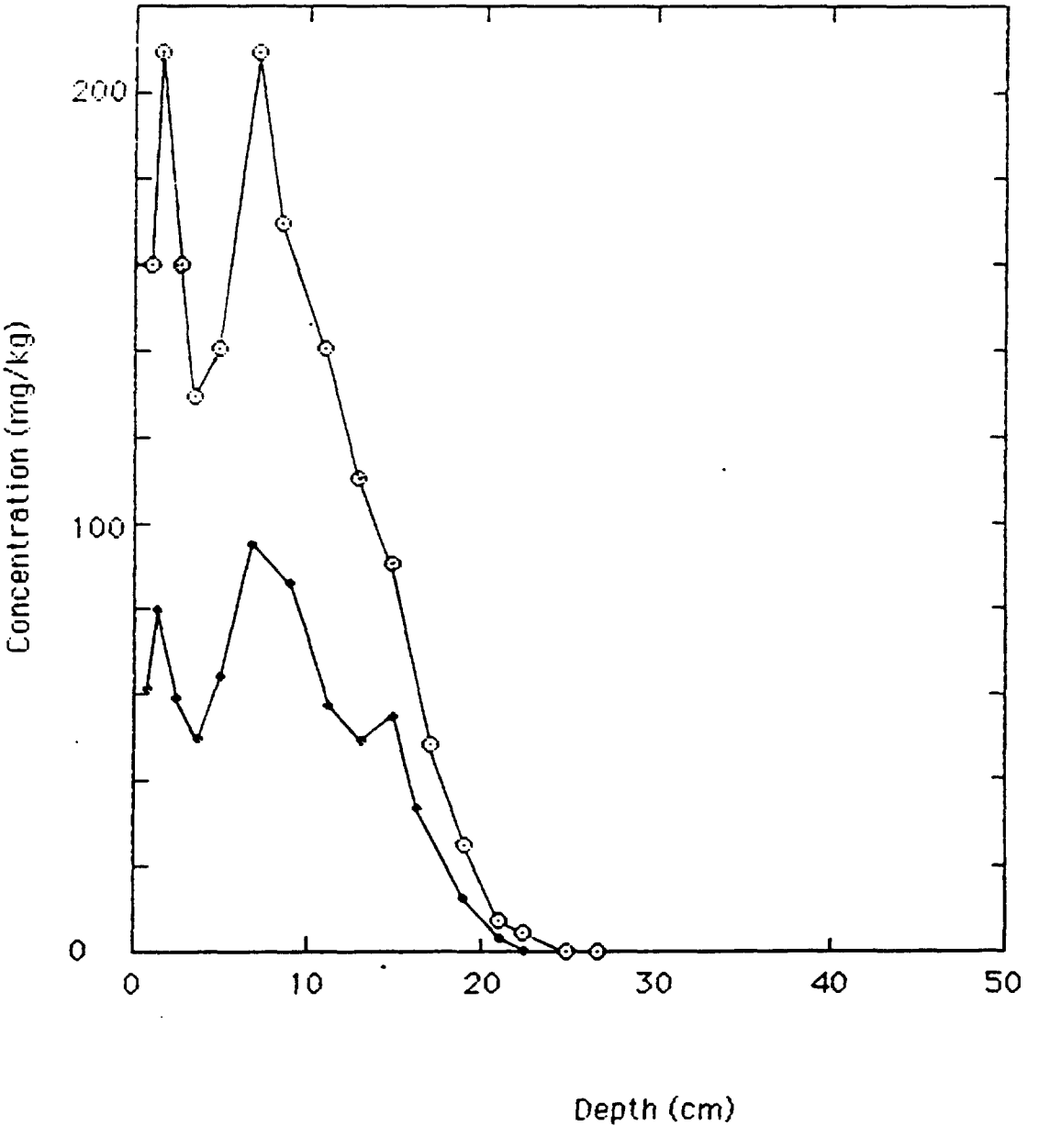
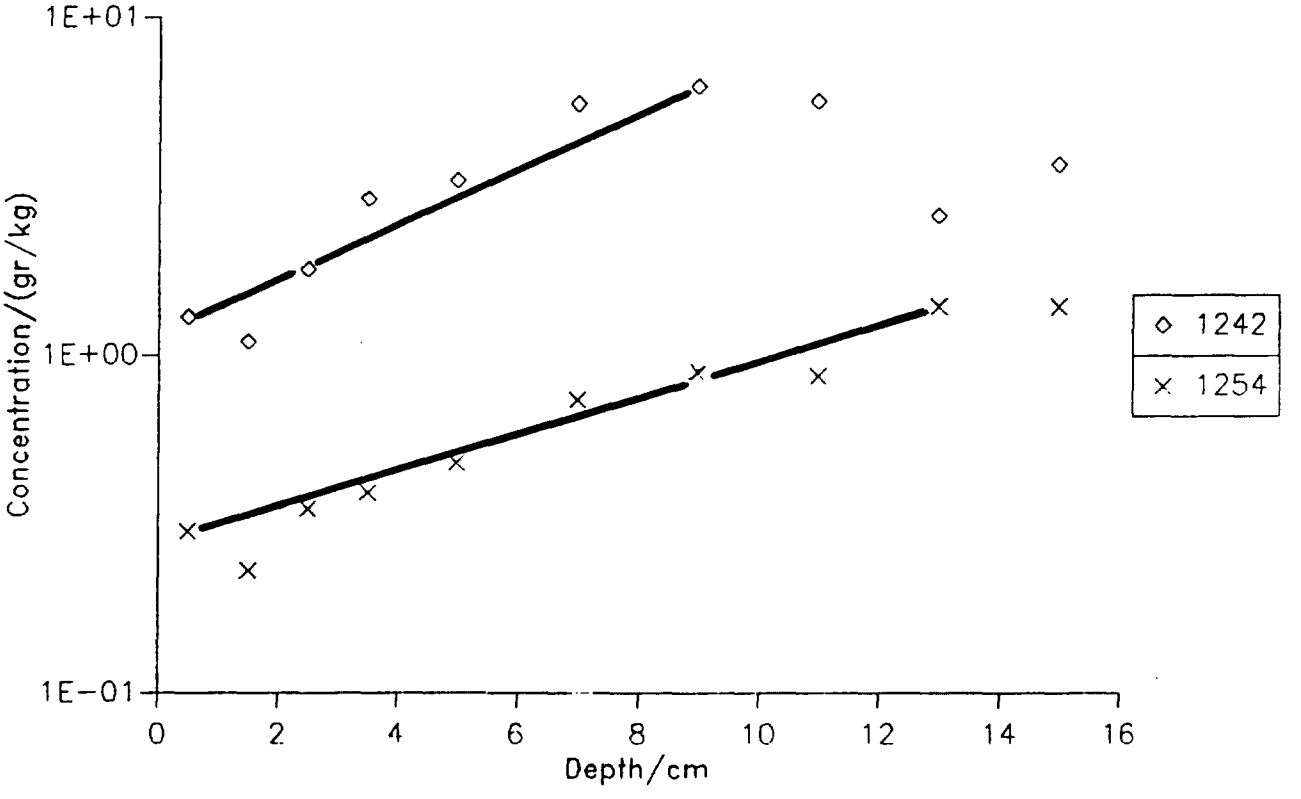


Figure 7. Concentration Profile at Balsam Site FX



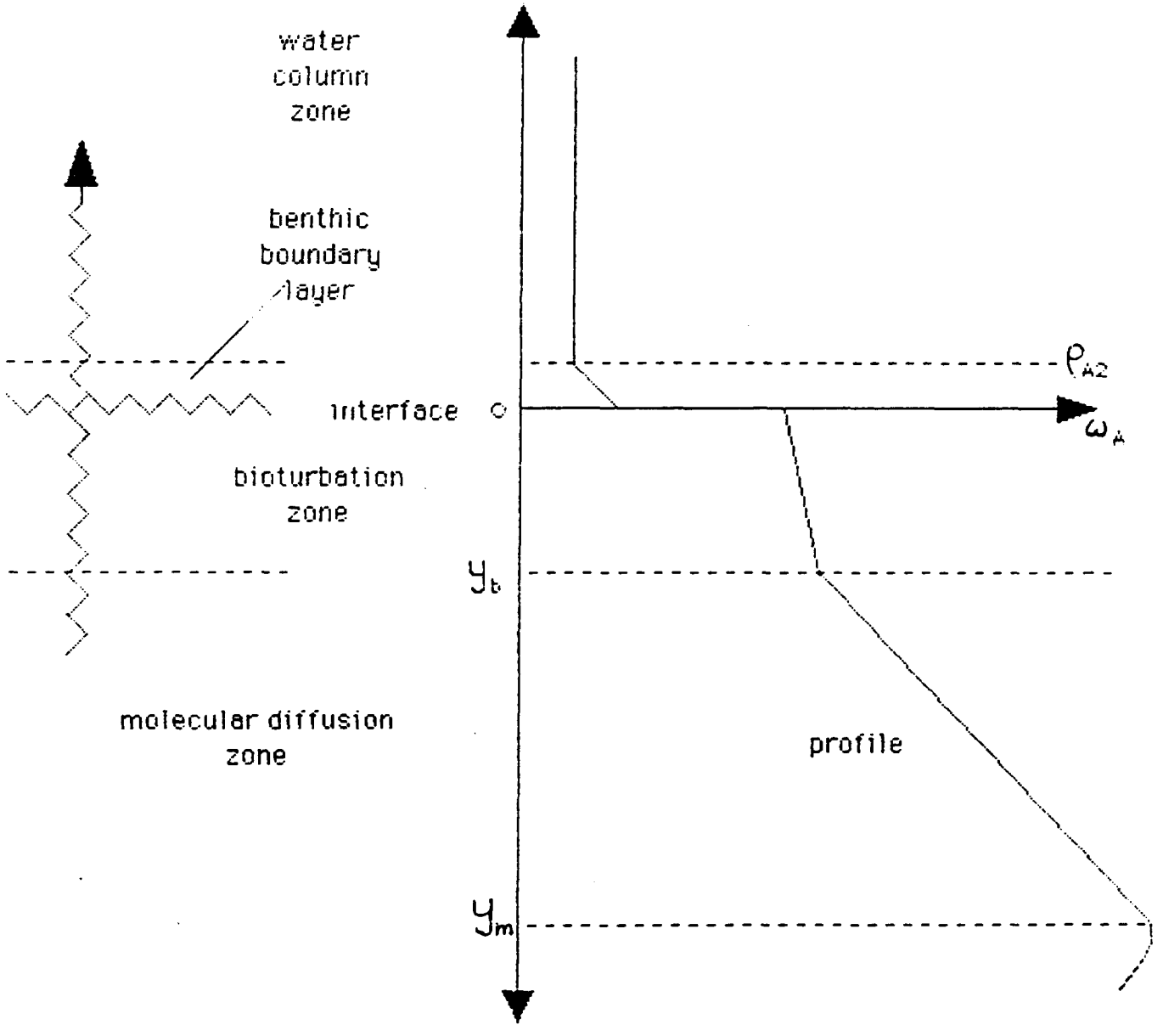


Figure 8 Transport Zones in Bed Sediment and Hypothetical Concentration Profile

Figure 9 Cumulative [illegible] PCB's Released-Summing [illegible] highly contaminated sediments in the range

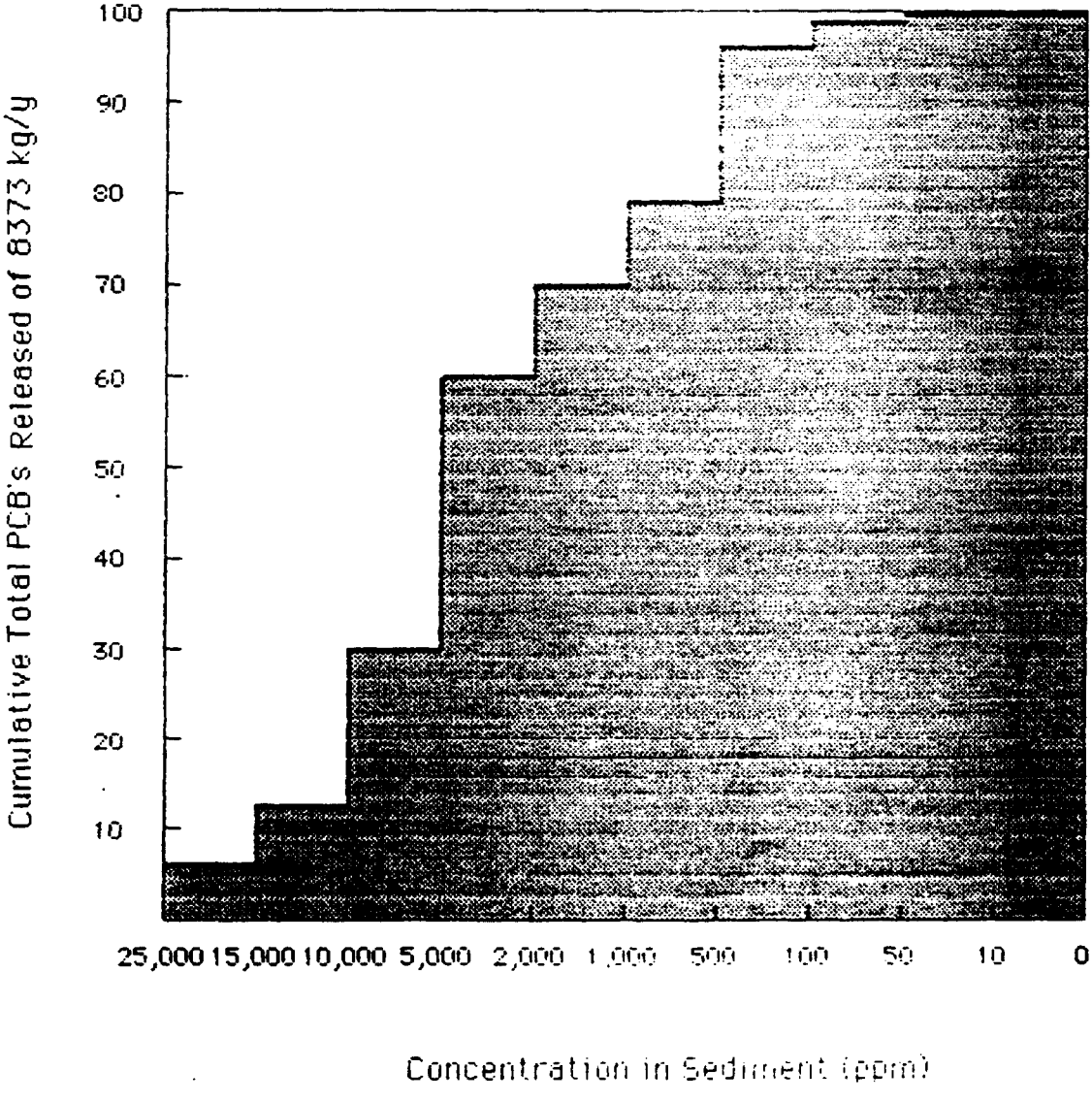


Figure 10 Cumulative Total PCB Release
vs. Cumulative Upper Estuary Surface Area

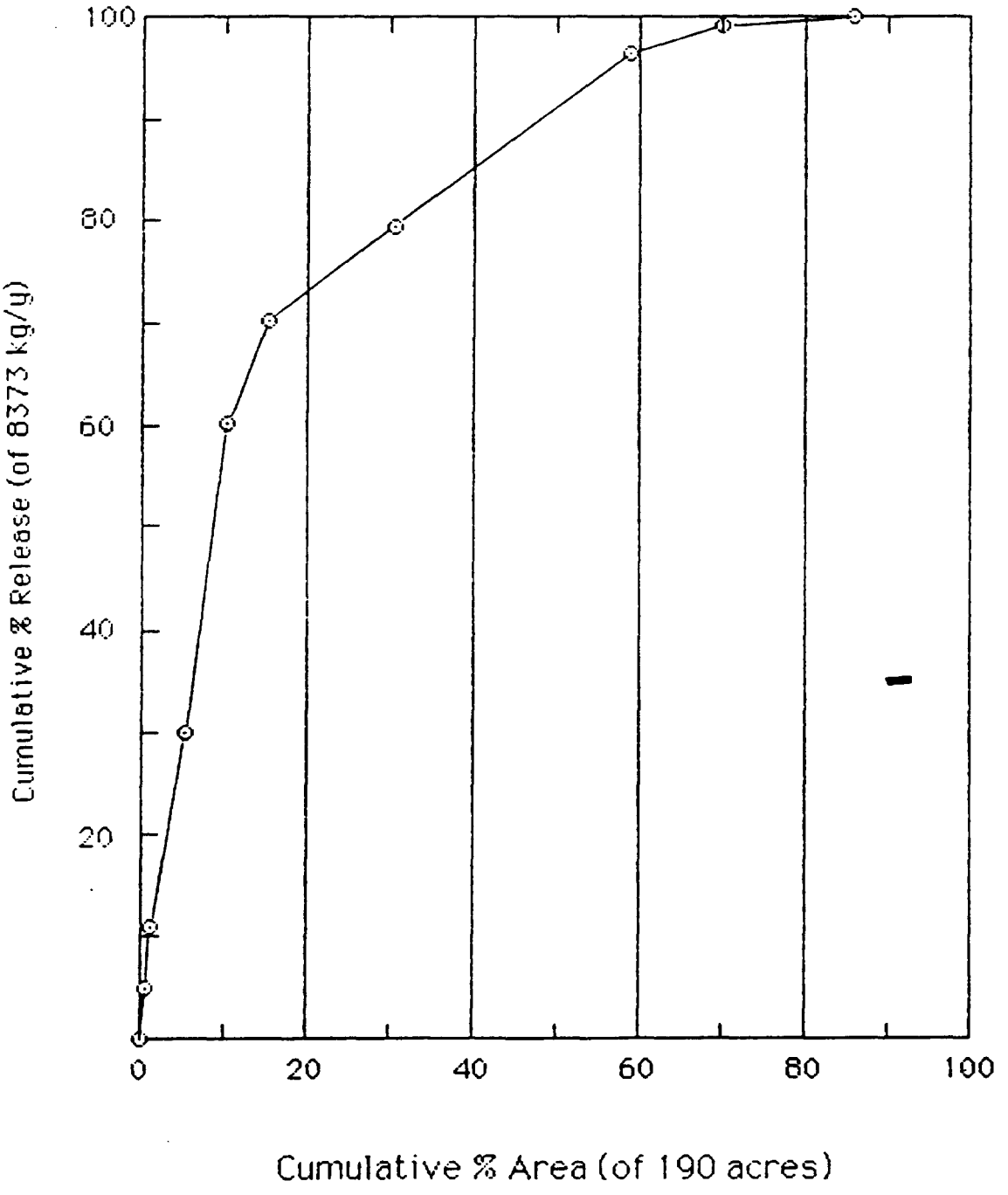


Figure 11 Incremental Total PCB Release
vs Cumulative Upper Estuary Surface Area

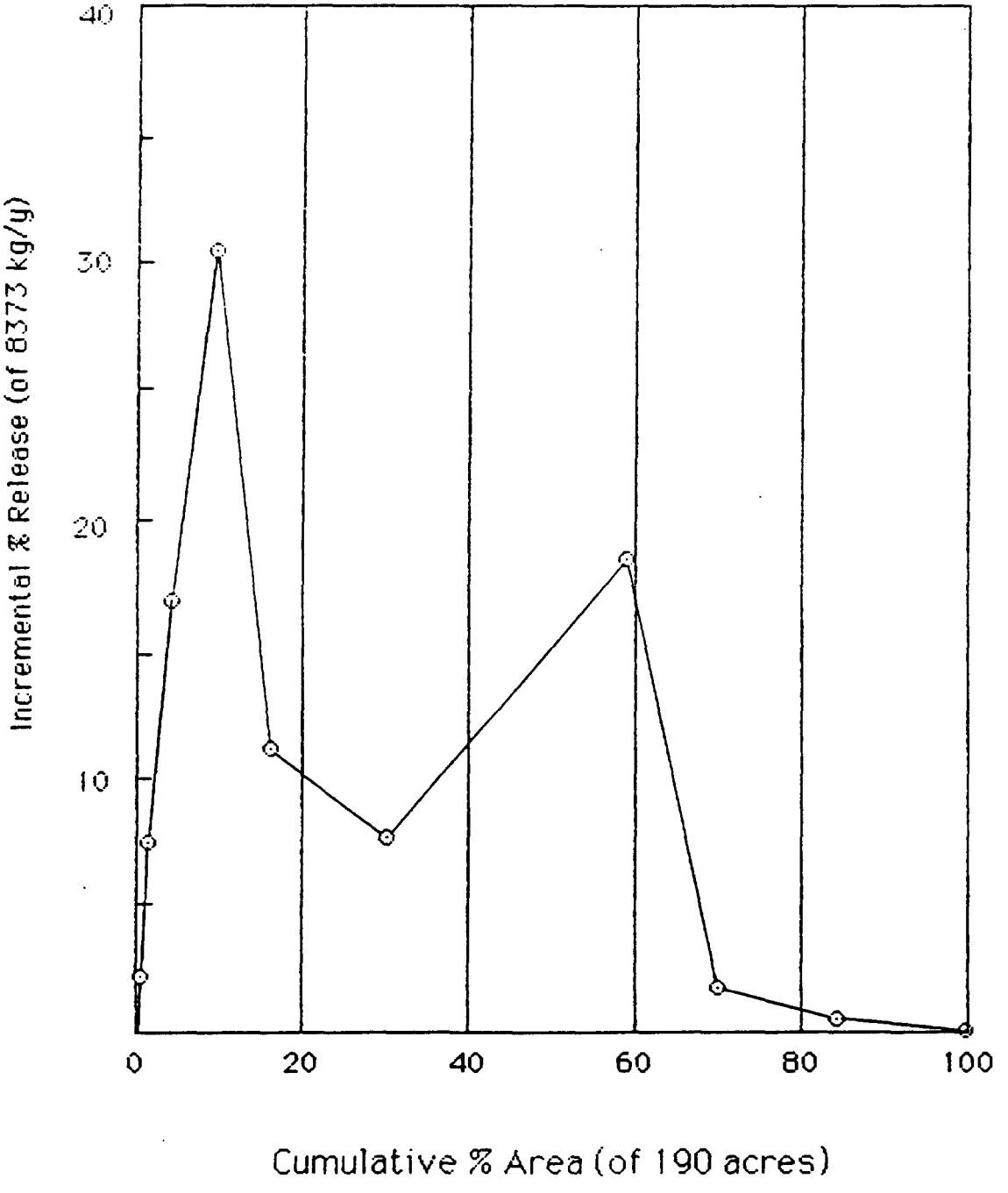
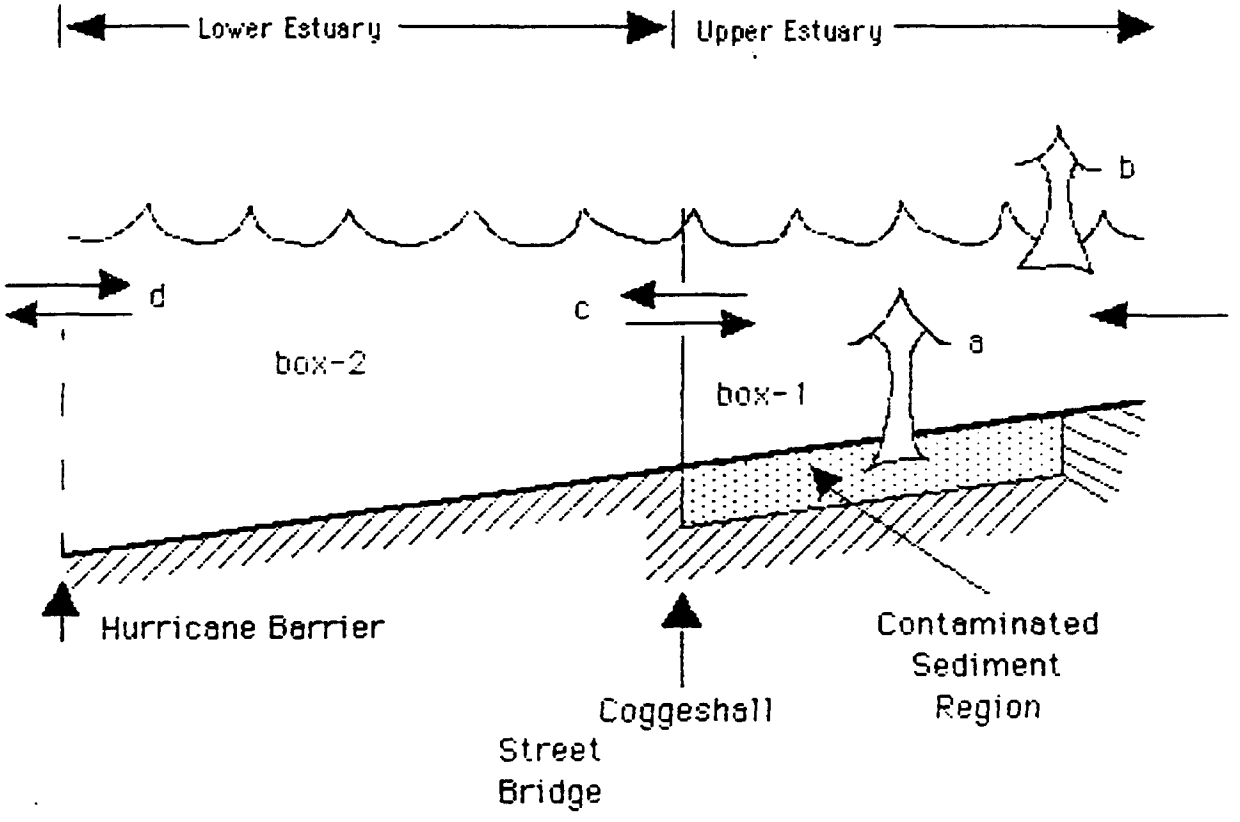


Figure 12
Conceptual Pathways for PCB
in the New Bedford Harbor



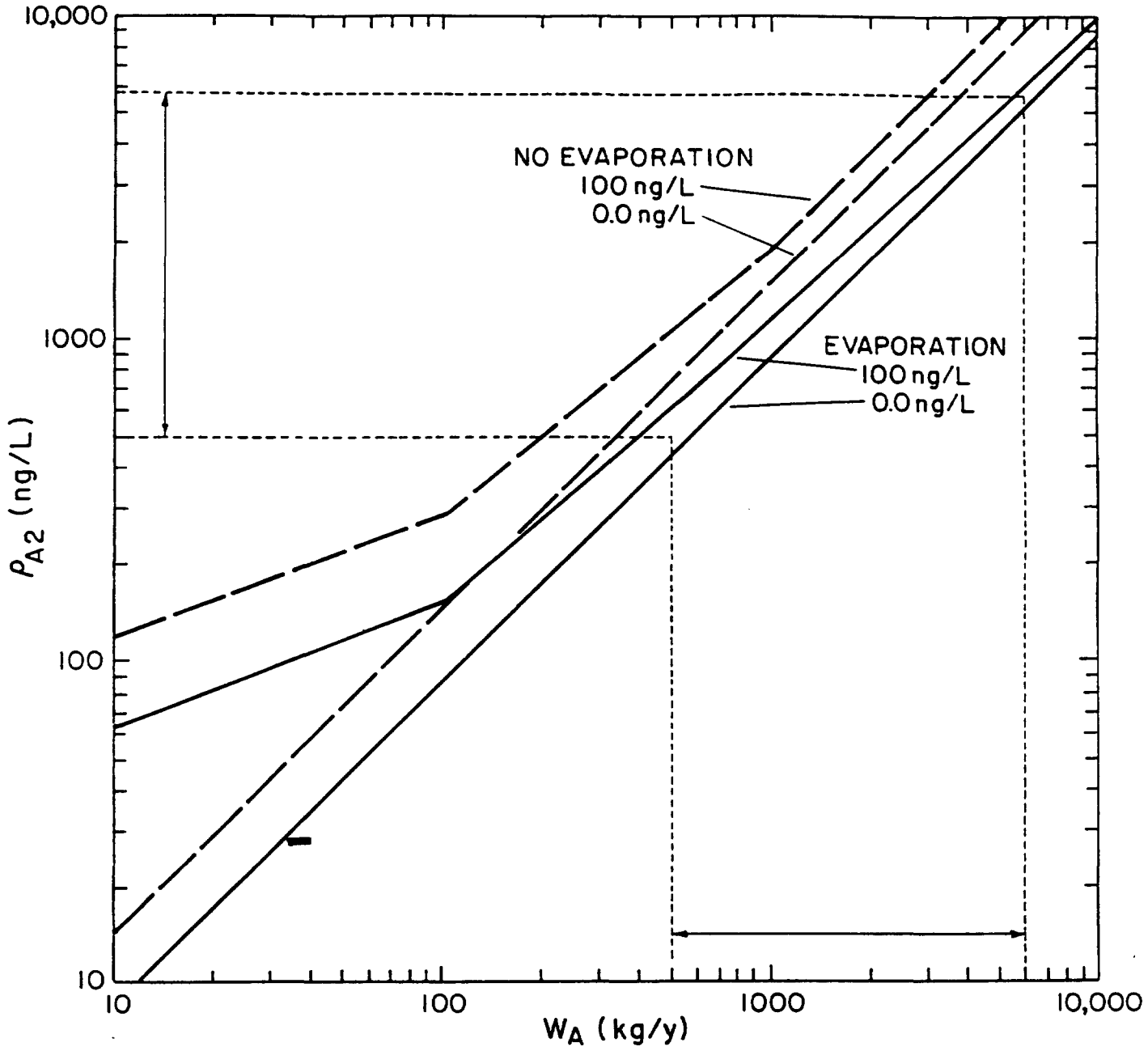


FIGURE 13. TOTAL PCB MASS BALANCE UPPER ESTURARY

Figure 14. PCB FLUX FROM UPPER ESTUARY-MODEL SUMMARY

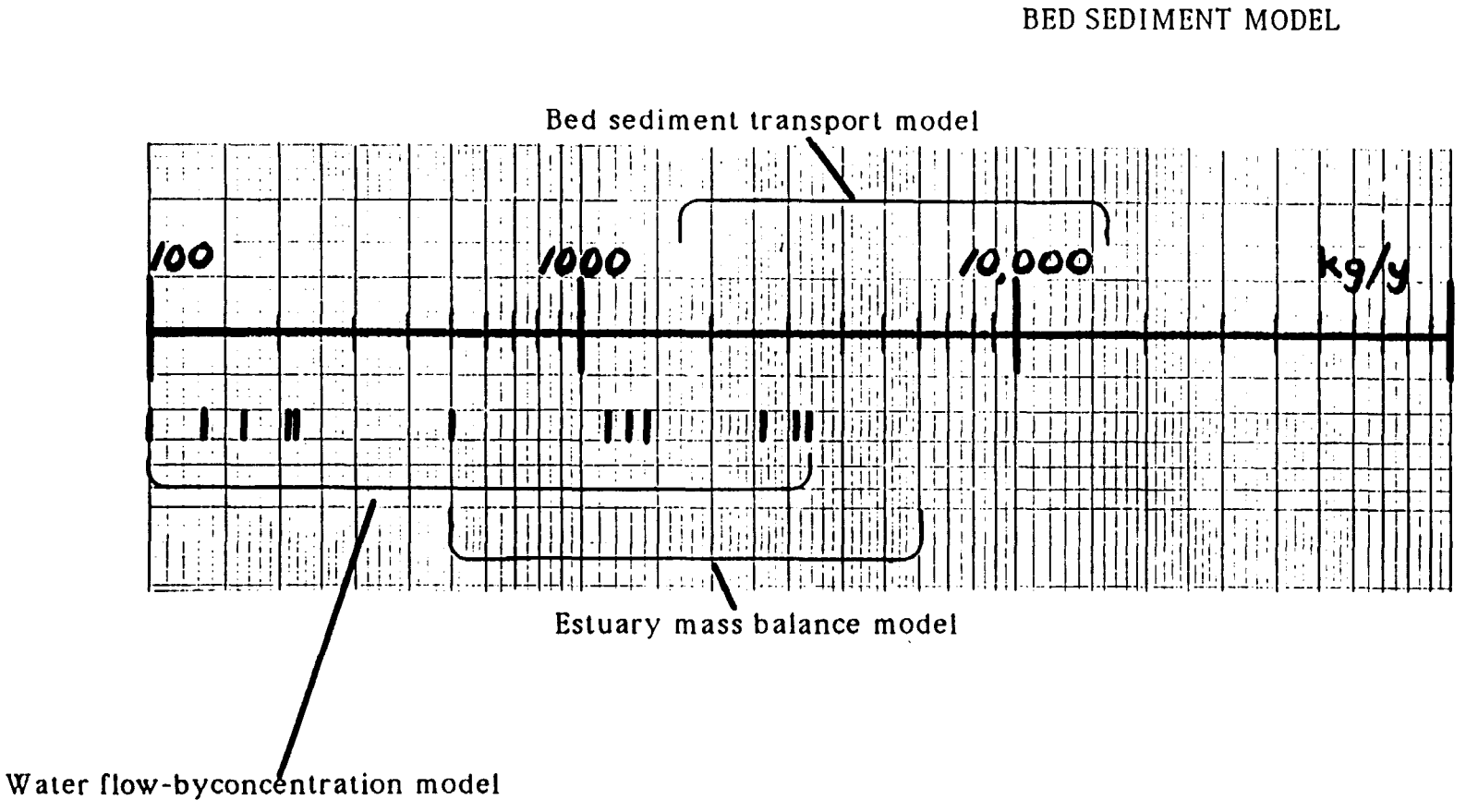
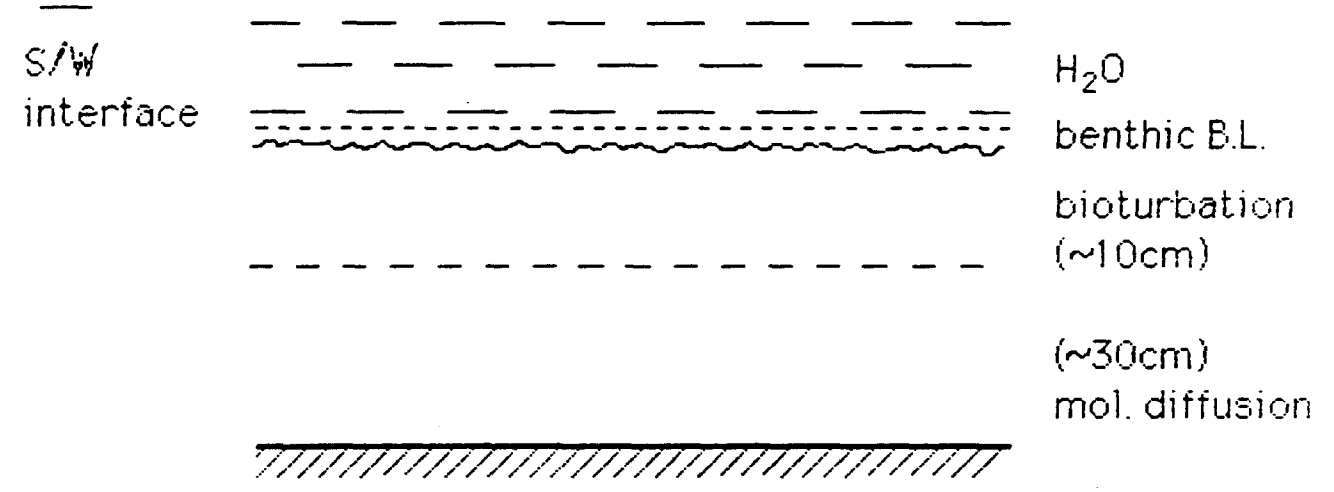
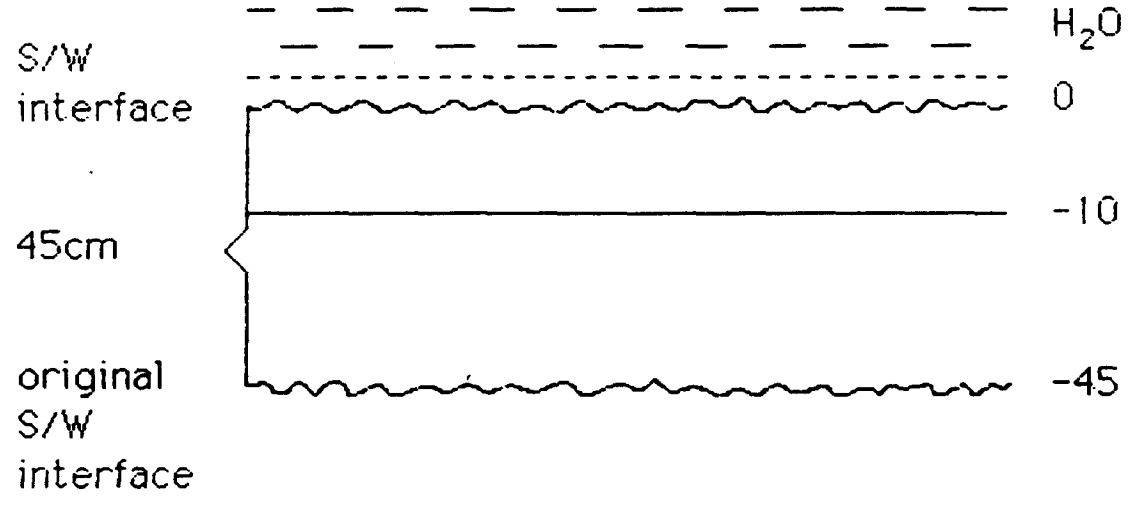


Figure 15
In-Situ Containment of Contaminated Bed Sediment

a. Un-Capped Contaminated



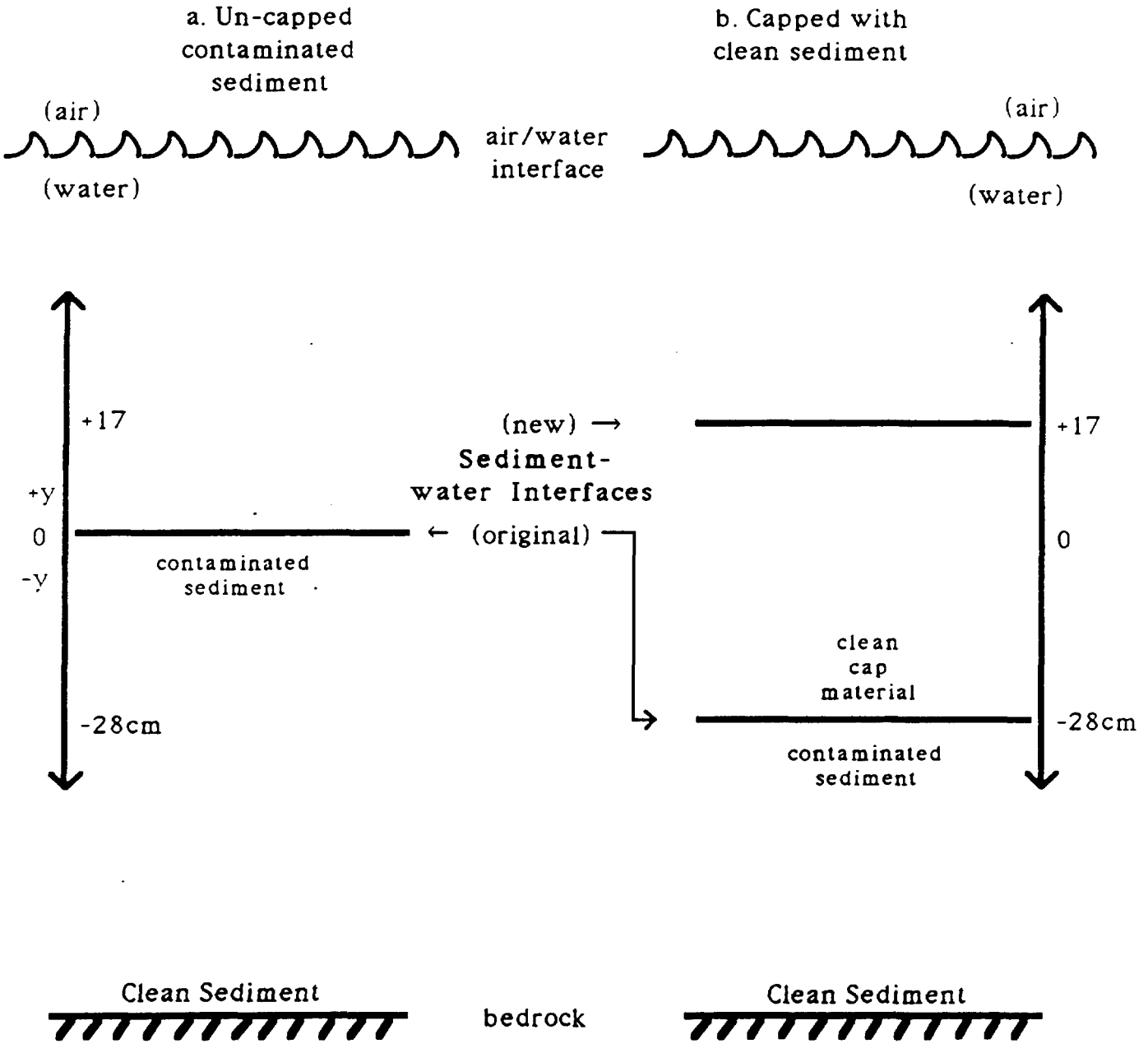
b. Capped with Clean Sediment



Contaminated Sediment

Figure 16

Bed Consolidation Following Capping



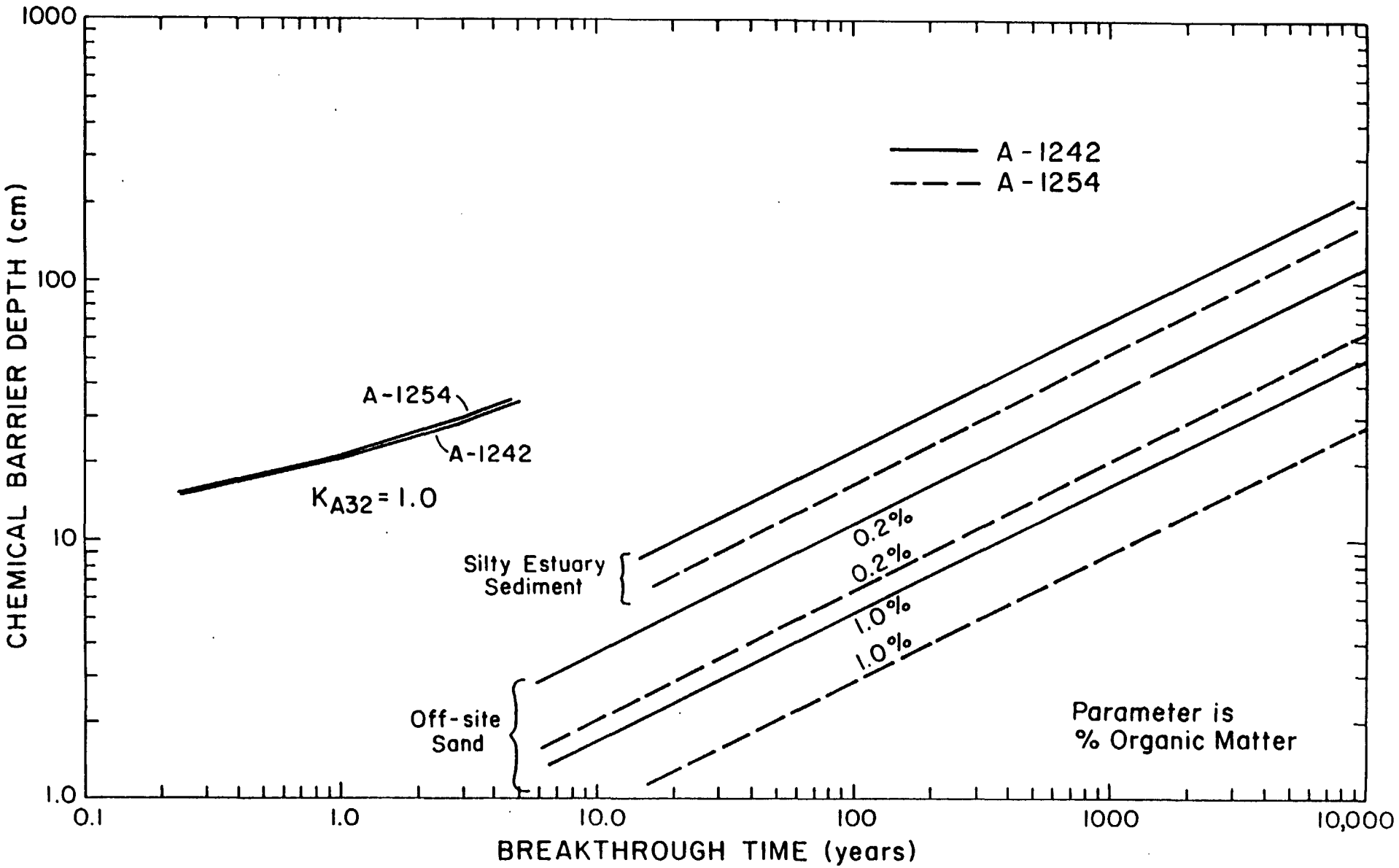


FIGURE 17. PCB BREAKTHROUGH TIME VS. BARRIER DEPTH

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APPENDICES

There are two appendices to this report and they commence on the next page.

APPENDIX A

Current (1989) PCB Fluxes Based on Thin Layer Sediment Samples Balsam Environmental Site FX

SUMMARY

As a result of industrial activities, New Bedford Harbor contains sediments contaminated with various polychlorinated biphenyls (PCBs). An attempt was made to estimate the current flux of PCBs from the sediment into the overlying water column. Fluxes were estimated by two different methods and fit to PCB profiles with depth at a single high concentration location (Balsam Environmental Consultants, site FX). In one model the flux was assumed proportional to the total mass in the profile and the difference between the PCB levels in the sediment in 1977 (assumed profile) and the observed PCB levels in 1989 was used to fit a first-order exchange coefficient. The other model assumed that bioturbation and deposition controlled the development of the concentration profile. An effective diffusion coefficient was fit to the observed concentration profile in this method. The estimated fluxes by the two modeling approaches agreed within a factor of 2.

Results indicate that the current flux of Aroclor 1242/1016 PCB out of the sediment can be approximately estimated with the equation,

$$1242/1016 \text{ Flux } (mg/cm^2 \cdot yr) = 0.917(10^{-3}) \ (\omega_{avg} - \omega_b) \ (mg/kg)$$

Here ω_{avg} is the 0-12" depth averaged concentration in the sediment and ω_b is the sediment concentration of Aroclor 1242 that would be in equilibrium with the overlying water column. The Aroclor 1254 PCB flux can be estimated by the equation,

$$1254 \text{ Flux } (mg/cm^2 \cdot yr) = 1.09 \ (10^{-3}) \ (\omega_{avg} - \omega_b) \ (mg/kg)$$

The recommended flux equations correspond to the more rigorous "enhanced diffusion" model of the PCB transport.

The current PCB fluxes were estimated from vertical profiles of Aroclor 1254 and 1242/1016 at a single site (Balsam Environmental Consutants Site FX). This is the only site where vertical profiles of PCB suitable for a flux analysis are available. The vertical profiles of PCB for this site are summarized in Table 1. Preliminary calculations indicated that molecular diffusion in the pore volume of the sediments was insignificant as a transport mechanism. The primary transport mechanism was instead attributed to be bioturbation of the near surface sediment layer and this process was analyzed using two different modeling approaches.

1) PCB loss rate from the sediment was proportional to the mass present, and

2) PCB loss rate from the sediment was described by a concentration gradient driven mechanism with a diffusion coefficient enhanced by bioturbation

Each of these models is discussed separately below.

1) Flux Proportional to Mass Present Model

This model is equivalent to assuming that bioturbation keeps the surface layer of the sediment well-mixed (at variance with the observed concentration profile at Site FX). At the time of the discontinuance of PCB emissions to New Bedford Harbor (assumed to be 1977, 12 years prior to the analysis), the PCB profiles were assumed uniform at the maximum concentration observed currently. The total mass in the vertical profile per unit surface area of sediment (M) at any time subsequent to 1977 was assumed given by

$$\frac{dM}{dt} = - K M \quad \text{or} \quad M = M_0 \, e^{-Kt} \tag{1}$$

M is equal to the mass concentration of PCB (ω, mg/kg) times the weight of sediment per unit area ($\rho_b d$, bulk density times depth, kg/cm^2). Writing this to solve for the unknown rate coefficient, K,

$$K = - 1/t \left[\ln \left\{ \frac{M - M_0}{M_0} + 1 \right\} \right] \tag{2}$$

From Table 1 for Aroclor 1242/1016, averaging over depth d=6 in ($\approx$15 cm)

$$\frac{M - M_0}{M_0} = \frac{3850(15) - 6300(15)}{6300\ (15)} = -0.389 \tag{3}$$

With t=12 years, this suggests that the rate constant for PCB transfer between the sediment and the overlying water column is 0.041 yr^{-1}. For Aroclor 1254, averaging over the top 15 cm (i.e. to the peak concentrations), K is about 0.051 yr^{-1}. The fluxes of the two PCBs are then given by

PCB 1242/1016:

$$\text{Flux}=K\ \omega_{avg}\ \rho_b\ d \qquad (4)$$

$$=(0.041yr^{-1})(3750mg/kg)(kg/1000g)(0.75g/cm^3)(15cm)$$

$$= 1.8\ \ mg/cm^2 \cdot yr$$

PCB 1254:

$$\text{Flux}= K\ \omega_{avg}\ \rho_b\ d \qquad (5)$$

$$= (0.051yr^{-1})(803mg/kg)(kg/1000g)(0.75g/cm^3)(15cm)$$

$$= 0.44\ mg/cm^2 \cdot yr$$

The PCB concentrations of the sediment are normally reported as a depth averaged concentration over 12". At Site FX, the 12" average PCB 1242/1016 concentration is 2,290 mg/kg while the 12" average PCB 1254 concentration is 760 mg/kg. With these average concentrations, Equations 4 or 5 suggest that the current flux of PCB 1242/1016 is 2.14 $gr/cm^2 \cdot yr$ and the flux for 1254 is 0.886 $gr/cm^2 \cdot yr$ for 1254. To estimate the fluxes using this approach at other sites where only the 12" average concentration (ω_{avg}) is known, the following formula can be used

$$\text{Flux}\ (mg/cm^2 \cdot yr)= \alpha\ (\omega_{avg}-\omega_b)\ (mg/kg) \qquad (6)$$

where $\alpha(=K\rho_b d)$ is 0.000937 for 1242/1016 and 0.00117 for 1254. ω_b is the PCB background concentration (suface sediment concentration).

2) Enhanced Diffusion Model

In this model, an effective diffusion coefficient is derived from the observed vertical concentration profile at Site FX. The peak concentration observed in the measured profile is assumed to represent a uniform initial concentration at time 0 (1977). During the period subsequent to 1977, mass was assumed lost by bioturbation in the sediment at a rate proportional to the PCB concentration gradient in the sediment. Also during this period, deposition of essentially clean sediment raised the sediment surface 0.5 cm/yr. Assuming that the enhanced diffusion coefficient is essentially constant throughout the contaminated depth, the governing equation

can be written

$$\frac{\partial \omega}{\partial t} + U \frac{\partial \omega}{\partial z} = D \frac{\partial^2 \omega}{\partial z \partial z} \qquad (7)$$

subject to

$\omega = 0$ $\quad z = 0$ (clean overlying water)

$\omega = \omega_0$ $\quad z \rightarrow \infty$ (deep sediment unaffected by bioturbation)

$\omega = \omega_0$ $\quad t = 0$ (sediment initially uniformly contaminated)

Carslaw and Jaeger (Conduction of Heat in Solids, 2nd Ed., 1959) give the solution to the equivalent heat transfer problem which can be written,

$$\omega = \omega_0 - \frac{\omega_0}{2}\left[\operatorname{erfc}\left\{\frac{z - Ut}{2\sqrt{Dt}}\right\} + \exp\left\{\frac{Uz}{D}\right\} \operatorname{erfc}\left\{\frac{z + Ut}{2\sqrt{Dt}}\right\}\right] \qquad (8)$$

Here z is the depth, U is the sediment deposition velocity (-0.5 cm/yr in a coordinate system such that the surface is always at z=0), D is an effective diffusion coefficient and t is time. Based on this model, the flux at z=0 (i.e. the sediment surface) can be shown to be

$$\text{Flux} = -D\frac{\partial \omega}{\partial z} = \frac{\omega_0 D}{2}\left[\frac{2}{\sqrt{\pi Dt}}\left[e^{\beta^2}\right] - \frac{U}{D}\operatorname{erfc}|\beta|\right] \qquad (9)$$

where

$$\beta = \frac{Ut}{2\sqrt{Dt}} \qquad (10)$$

For the purposes of the fit of the model equation to the experimental profile at Site FX, the measured average concentration between two levels was assumed to be a point value at the midpoint of the interval (e.g. 8-10 cm sample concentration was assumed to apply at z=9cm). ω_0 was taken to be the maximum observed concentration in the sediment and only those data from points $z \leq z(\omega_0)$ were used to fit the model equation to the data. The best fit effective diffusivity for Aroclor 1242/1016 was 3.36 cm^2/yr and for Aroclor 1254 was 7.1 cm^2/yr. Separate analysis of particle diffusion using radioisotopes has indicated a particle diffusion coefficient of about 9.5 cm^2/yr, in good agreement with the observed PCB effective diffusivities.

Using the fitted effective diffusivity, the predicted flux of Aroclor 1242/1016 from the sediment at Site FX is about 2.89

$mg/cm^2 \cdot yr$ and the predicted flux of Aroclor 1254 is about 0.763 $mg/cm^2 \cdot yr$. These estimates are quite close to the estimates made by assuming flux is proportional to mass present (Approach 1).

Another illustration of the validity of the model can be seen in the comparison of the model concentration predictions for Site FX with the observed data. For this purpose the concentrations at depths greater than $z=z(\omega_0)$ were estimated by assuming that they were the result of bioturbation driven "diffusion" onto the sediment prior to 1977. Due to the approximate symmetry of the observed concentration profiles at Site FX it was assumed that the same enhanced diffusion coefficient defined above would be appropriate and that the transient contamination period was approximately equal to the current decontamination period (i.e. 12 years). After 1977, the deep layers below $z=z(\omega_0)$ (i.e. below the observed maximum concentration) were assumed to be unifluenced by bioturbation while the upper layers (contaminated at the "steady state" concentration level, ω_0) lost PCBs by the enhanced diffusion mechanism. During the entire period, deposition at the rate of 0.5 cm/yr was assumed to occur. Given the current concentration versus depth profile, this deposition rate and the model described above suggest that significant PCB contamination began 40-50 years ago, consistent with the actual contamination history. The comparison of this model with the observed concentration profiles can be found in Figure 1. The agreement is excellent.

Since only depth-averaged concentrations are reported for sites other than Site FX, ω_0 must be estimated without fitting a diffusivity to a profile. If the concentration profiles over the top 12" of sediment were to increase linearly from zero deep within the sediment and decrease linearly to zero at the surface of the sediment, the maximum concentration (and therefore, by assumption, ω_0) would be twice the average concentration. The effective diffusivity estimated from the Site FX data and this procedure for the estimation of ω_0 allows an estimation of the flux from any New Bedford Harbor site.

Using this approach, the flux of Aroclor 1242/1016 PCB out of the sediment can be approximately estimated with the equation,

$$1242/1016 \text{ Flux } (mg/cm^2 \cdot yr) = 1.09(10^{-3})(\omega_{avg}-\omega_b) \text{ } (mg/kg) \quad (11)$$

Here ω_{avg} is the 0-12" depth averaged concentration in the sediment and ω_b is the sediment concentration that would be in equilibrium with the background water concentration. This equation is derived from Equations 9 and 10 using the previously defined parameters and with $\omega_0=2\omega_{avg}$. Similarly, the Aroclor 1254 PCB flux can be estimated by the equation,

$$1242/1016 \text{ Flux } (mg/cm^2 \cdot yr) = 0.917(10^{-3})(\omega_{avg}-\omega_b) \text{ } (mg/kg) \quad (12)$$

These formulas calculate the flux for Aroclor 1254 to within 9% of the full model (i.e. using the actual concentration profile rather than the average) and the flux for Aroclor 1242/1016 to within 22% of the full model. Thus the above equations are recommended for use with other sites to estimate current PCB flux.

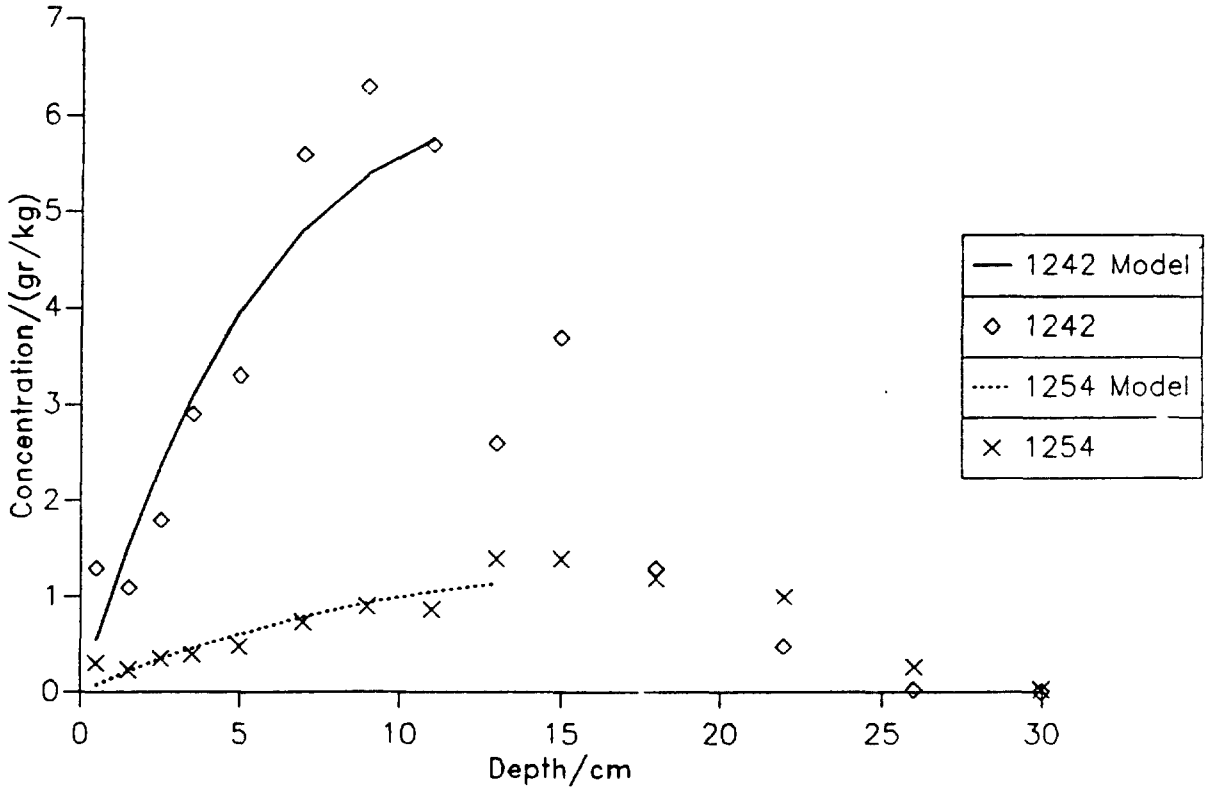
A summary of the various model predictions for PCB flux can be found in Table 2 below.

Table 2
Comparison of Predictions of Models of PCB Fluxes
Site FX

	PCB Flux $mg/cm^2 \cdot yr$ 1242/1016	1254
1) Flux = -K M		
Equations 4,5	1.80	0.44
Equation 6	2.14	0.89
2) Flux = $-D\frac{\partial \omega}{\partial z}$		
Equation 9	2.89[1]	0.76[1]
Equations 11,12	3.53	0.83

[1]Considered the most rigorous estimate when profile information is available.

Figure 1. Concentration Profile at Balsam Site FX



APPENDIX B

PCB Fluxes after Capping with Clean Sediment

SUMMARY

The mobility of PCBs in New Bedford Harbor sediment after capping with 45 cm of clean sediment was estimated. PCB transport was assumed to occur via pore diffusion in the stagnant lower 35 cm of the capping layer and by bioturbation induced mixing in the top 10 cm. Only 4-14% of the PCB mass was estimated to have moved from the current sediments after 10,000 years, allowing the concentration at the bottom of the capping layer to be treated as constant. The mass transfer resistance in the layer mixed by bioturbation was approximately 1000 times less than in the stagnant capping layer, suggesting that the PCB concentration at the bottom of the bioturbation zone was essentially zero. It was estimated that 1550-62000 years was required to achieve concentrations in the bioturbation layer that exceed 0.01% of the current sediment concentration. A higher organic carbon content capping layer significantly increases the time till PCB breakthrough and time to steady state.

The steady state PCB flux after capping with a 45 cm layer of clean sediment is between 51000 and 93000 times less than the current flux at the Balsam Environmental Site FX. Steady state fluxes through the capping layer can be estimated at other sites with the formula

$$\text{Flux } (mg/cm^2 \cdot yr) = 0.000639\ \rho_0 \quad (mg/L)$$

where ρ_0 is the pore water concentration of PCB in the current sediment. The time required to achieve steady state (as determined by the time required to achieve 95% of the steady state flux) varied between 78500 years for Aroclor 1242 in a 0.2% organic carbon (OC) capping layer, and 100,000 years for Aroclor 1254 in a 1% organic carbon capping layer. After 10,000 years, the fluxes ($mg/cm^2 \cdot yr$) of PCB from the capped sediments can be estimated with the equations

Aroclor 1242	w/1% OC cap	$\text{Flux} = 1.027(10^{-4})\ \rho_0$	(mg/L)
	w/0.2% OC cap	$\text{Flux} = 6.109(10^{-4})\ \rho_0$	
Aroclor 1254	w/1% OC cap	$\text{Flux} = 1.14(10^{-6})\ \rho_0$	(mg/L)
	w/0.2% OC cap	$\text{Flux} = 3.80(10^{-4})\ \rho_0$	

It has been proposed to reduce the PCB concentrations in the New Bedford Harbor by capping the contaminated sediments with clean sediment. The cap could pose a significant barrier to PCBs currently adsorbed to the sediment and could make the overlying water essentially free of PCBs without removal of the contaminated sediment. The purpose of the present evaluation is to determine the potential reduction of PCB flux from the sediments by capping.

The capped layer is assumed to be 45 cm of clean sediment. The specific capping sediment to be employed has a porosity of about 0.25, a dry bulk density of 1.19 gr/cm^3 and an organic carbon content of between 0.2 and 1%. Employing the organic carbon sediment water partition coefficient for Aroclor 1242 and Aroclor 1254 and correcting for water salinity, the partition coefficient (K_d) for a sediment containing 1% organic carbon is 1980 and 4811 for the two Aroclors, respectively. The corresponding numbers for a capping sediment of 0.25% organic carbon are 396 and 1962 for Aroclor 1242 and Aroclor 1254, respectively. The total mass of PCB in the capping sediment is given by the sum of the mass in the fluid-filled pore spaces and the mass adsorbed to the sediment.

$$\text{Mass} = (\varepsilon + \rho_b K_d)\ (\rho)\ (\text{Volume of sediment}) \qquad (1)$$
$$= \varphi\ \rho\ V$$

where ε is the porosity of the capping sediment, ρ_b is the bulk density of the sediment and ρ is the mass concentration of PCBs in the interstitial fluid of the sediment (mg/L). φ is the ratio of the total mass of PCB in the sediment to the mass of PCB in the interstitial fluid.

If it is assumed that the capping layer of clean sediment is undisturbed, the PCB will move from the currently contaminated sediment by diffusion. The molecular diffusion coefficient of the PCB in water is reduced in this process by the fraction of pore space available for flow, the tortuosity of the pore spaces and the adsorption of PCB onto the clean sediment. That is, the effective diffusion coefficient for the process is given by

$$\mathcal{D}_{eff} = \frac{\mathcal{D}\ \varepsilon^{4/3}}{(\varepsilon + \rho_b\ K_d)} = \frac{\mathcal{D}\ \varepsilon^{4/3}}{\varphi} \qquad (2)$$

Here $\varepsilon^{4/3}$ is assumed to describe both void fraction and tortuosity effects. At steady state, the flux through the capping layer as defined by this mechanism is given by

$$\text{Flux}|_{cap} = -\mathcal{D}_{eff} \frac{\partial \rho}{\partial z} \varphi = \mathcal{D}_{eff} \varphi (\rho_0 - \rho_1)/\ell \qquad (3)$$

$$= K_{cap} (\rho_0 - \rho_1)$$

Here ρ_0 is the pore water concentration at the interface of the capping layer with the current sediment, ρ_1 is the pore water concentration at the top of the diffusion controlled capping layer and ℓ is the effective length of the capping layer. K_{cap} varies between 0.638 cm/yr for Aroclor 1242 and 0.681 cm/yr for Aroclor 1254. Note that the steady state pore diffusion fluxes are independent of sediment-water partition coefficient and the capping sediment organic carbon if local equilibrium is assumed.

Diffusion would dominate only in the lower 35 cm of capping sediment in that the upper 10 cm would be influenced by bioturbation. As shown by the analysis of current fluxes, which are dominated by bioturbation, the effective bioturbation diffusion coefficient based on particle concentration, D, is about 10 cm^2/yr. At steady state, the flux in the bioturbed zone is given by

$$\text{Flux}|_{bio} = - D \frac{\partial \omega}{\partial z} = D(\omega_1 - \omega_2)/\ell_{bio} \qquad (4)$$

Note that the bioturbation flux is based on ω, the dry basis solid PCB concentration, since the effective diffusion coefficient for bioturbation defines the rate of particle movement in the bed. To base the flux on the pore water concentration, the concentrations must be multiplied by the sediment-water partition coefficient, or

$$\text{Flux}|_{bio} = \frac{D}{\ell_{bio}} K_d \rho_b (\rho_1 - \rho_2) \qquad (5)$$

$$= K_{bio} (\rho_1 - \rho_2)$$

Here, ρ_b is the dry bulk density of the capping sediment and ρ_2 is the pore water concentration at the top of the bioturbation layer (i.e. the exposed capping layer surface). K_{bio} varies between 6414 cm/yr for Aroclor 1254 with a 1% organic carbon capping layer to 471 cm/yr for Aroclor 1242 with a 0.2% organic carbon capping layer.

The flux of PCB from the sediment is also limited by the resistance of the water-side film. The steady-state flux through this layer is given by

$$\text{Flux}|_{film} = K_{film} \ (\rho_2 - \rho_3) \qquad (6)$$

where ρ_3 is the background water concentration of PCBs. Due to the reduction in flux posed by the capped layer and regulation of potential sources of PCBs, this will be assumed essentially 0. K_{film} is approximately 2.1 cm/hr or 17500 cm/yr based on benthic boundary layer correlations which are likely to overestimate the film resistance in the shallow harbor.

These mass transfer resistances act in series and the overall resistance at steady state can be determined from the equation

$$\text{Resistance} = \frac{1}{K_{eff}} = \frac{1}{K_{cap}} + \frac{1}{K_{bio}} + \frac{1}{K_{film}} \qquad (7)$$

This equation suggests that pore diffusion through the stagnant portion of the capping layer (the lower 35 cm) clearly dominates the total resistance. Thus the concentration at the top of the stagnant capping layer can be taken as ρ_3, the background water concentration (assumed zero). The bioturbation layer and the overlying water film can be assumed quasi-steady and the flux estimated in the stagnant capping layer can be used to estimate a concentration in the bioturbation zone. The effective mass transfer coefficient of the water film and bioturbation layer varies between 459 cm/yr for Aroclor 1242 with a 0.2% organic carbon capping layer and 4700 cm/yr for Aroclor 1254 with a 1% organic carbon capping layer.

The movement of the PCB through the controlling stagnant capping sediment is then described by

$$\frac{\partial \rho}{\partial t} = \mathcal{D}_{eff} \frac{\partial^2 \rho}{\partial z \partial z} \qquad (8)$$

subject to

$\rho = 0 \quad z = \ell$ (neglect resistance of bioturbation layer)

$\rho = \rho_0 \quad z = 0$ (constant concentration at current sediment)

$\rho = 0 \quad t = 0$ (initially clean capping sediment)

Carslaw and Jaeger (Conduction of Heat in Solids, 1959) give the solution to the equivalent heat transfer problem to be

$$\rho = \rho_0 - \rho_0 \frac{z}{\ell} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\rho_0}{n} \sin\frac{n\pi z}{\ell} \exp\left\{-\mathfrak{D}_{eff} n^2 \pi^2 t/\ell^2\right\} \qquad (9)$$

The corresponding flux from the exposed surface of the capping sediment is given by

$$\text{Flux} = -\varphi \mathfrak{D}_{eff} \frac{\partial \rho}{\partial z}$$

$$= \frac{\varphi \rho_0 \mathfrak{D}_{eff}}{\ell}\left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left\{-\mathfrak{D}_{eff} n^2 \pi^2 t/\ell^2\right\}\right] \qquad (10)$$

The steady state flux can be found directly or by taking the limit of Equation 10 as $t \to \infty$. The result is

$$\text{Flux} = \varphi \mathfrak{D}_{eff} \rho_0/\ell \qquad (11)$$

These equations assume that the concentration at z=0, the current sediment-water interface, is constant. This is true only if the mass lost by diffusion through the capping layer is small compared to the mass initially present. Integration of Equation 17 over time gives the total mass lost per unit area. At steady state, or for $t \approx 3\ell^2/(\mathfrak{D}_{eff}\pi^2)$, the mass lost is given by

$$\text{Mass/area} = 6.3 \left\{ \frac{\varphi \ell \rho_0}{\pi^2} \right\} \qquad (12)$$

Here steady state is defined as the time required to reach 95% of the steady state flux and varies from 7850 years for Aroclor 1242 with a 0.2% organic carbon capping layer and 100,000 years for Aroclor 1254 with a 1% organic carbon capping layer. The initial mass in the current sediment from a 0-12" average concentration measurement is $\rho_0 K_d \rho_b d = 181\ \rho_0$ mg/cm^2 for Aroclor 1242 and 493 ρ_0 for Aroclor 1254. Comparing the initial mass to the mass lost by the time of attainment of steady state indicates that only 5.8% of the mass of either PCB is lost by this time with a capping layer that is 0.2% organic carbon but that 29.1% is lost with a capping layer that is 1% organic carbon. If the initial concentration exceeds the solubility limit of the PCB in the seawater (.088 mg/L for 1242, 0.012 mg/L for 1254), for example at Balsam Site FX, the fraction of mass lost by the attainment of steady state will be even less. The fraction of mass lost will also be small at times less than those required to achieve steady state. The fractional mass lost at 10,000 years is 4-14% depending on the PCB and the organic carbon content of the cap. For much of the time of interest, therefore, the concentration can be assumed constant in the current sediment.

With this approximation, the steady-state flux of PCBs is given by Equation 11. For Balsam Environmental Site FX, the current pore water concentration is the water solubilities of 0.088 mg/L for Aroclor 1242 and 0.012 mg/L for Aroclor 1254. The flux of Aroclor 1242 with a capping layer that is 1% organic carbon is

$$\text{Flux}|_{1242} = \varphi_{1242}\, \mathcal{D}_{eff}\, \rho_0/\ell \qquad (14)$$

$$= (2356)(0.0095 cm^2/yr)(0.088 mg/L)(L/1000 cm^3)/35 cm$$

$$= 5.6\ (10^{-5})\ mg/cm^2 \cdot yr$$

This flux is more than 51,000 times smaller than the uncapped PCB flux of 2.89 $mg/cm^2 \cdot yr$ at the same site. In addition, the time to achieve 95% of this steady state flux is 39,200 years. At 10,000 years after capping, the flux is given by

$$\text{Flux} = \frac{\varphi \rho_0 \mathcal{D}_{eff}}{\ell}\left[\, 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left\{-\mathcal{D}_{eff} n^2 \pi^2 t/\ell^2\right\}\right] \qquad (15)$$

$$= 5.6(10^{-5})\ mg/cm^2 \cdot yr \quad \left[\, -e^{-0.765} + e^{-4(0.765)} - \ldots .\right.$$

$$= 9.04(10^{-6})\ mg/cm^2 \cdot yr$$

Site FX fluxes at steady state and after 10,000 years are summarized in Table 1 for both PCBs and capping layer organic contents.

Equation 10 can also be used to estimate concentrations in the bioturbation layer when it is recognized that the flux estimated by Equation 10 must be driven through that layer by a small but non-zero concentration gradient. The concentration in the bioturbation layer is approximately given by

$$\rho_{bio} \approx \rho_1 = \text{Flux} \left\{ \frac{1}{K_{bio}} + \frac{1}{K_{film}} \right\} \qquad (16)$$

The time required to achieve a concentration in the bioturbed zone that is 0.01% (1/10000) of the current sediment concentration is also given in Table 1.

Table 1

PCB Fluxes from Capped Sediments
Site FX

PCB/Cap OC**	Fluxes ($\mu g/cm^2 \cdot yr$)* Uncapped	Capped Steady	Capped 10,000 yrs	Time (yrs) to $\rho_1 = 0.0001 \rho_0$
Aroclor 1242				
1% OC	2890	0.0562	0.00904	13600
0.2% OC	2890	0.0562	0.00538	1550
Aroclor 1254				
1% OC	763	0.0082	0.000014	62000
0.2% OC	763	0.0082	0.000456	5280

* 1 $mg/cm^2 \cdot yr$ = 1000 $\mu g/cm^2 \cdot yr$

** OC = Organic carbon content of capping layer